Iso-Specific Ziegler-Natta Polymerization of α-Olefins with a Single-Component Organoyttrium Catalyst

Thesis by

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For My Parents

First of all I want to thank John Bercaw for giving me the opportunity to join his research group. Working with El Queso Grande has been a fantastic experience. I have learned much about the beauty of chemistry from him. Very few graduate students get the opportunity to work with an advisor who not only challenges and encourages them, but also cares about them as a person. It really makes the whole graduate experience all that much better.

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Physically Caltech is much like any other graduate school, everyone basically has the same equipment and facilities, however, it is the people that make this a special place. I have been truly fortunate to have been surrounded by a group of outstanding colleagues. I want to thank all the members of the Bercaw group both past and present for all of their help and support. Warren Piers created such a lasting impact upon the group that a piece of glassware was named in his honor . Andy Herring although he probably won't ever be able to straighten his middle finger properly did on occasion get his point across. Dave Lyon will always be remembered fondly for having a pot of coffee ready first thing in the morning, and always filling traps. LeRoy Whinnery deserves the sealed lips award for never telling Jim Toth. I have had the pleasure of knowing Donnie Cotter since the fall of 1984, and since this time he has been a great friend and excellent hiking companion. He may not know it, but he has been a real role model these past few years. Both Gui Bazan and Gerrit Luinstra helped me expand my

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Sandi Burkett has made the last two years truly special. My family has always been a constant source of love and encouragement. I know that as far as I have come is due to the *Windrow Philosophy* and the unending support from of my sisters Kathleen and Bridget, and my Mother and Father. I wish to dedicate this thesis to my parents who I know won't understand what I've written, but will know what I mean when I say I NUM MOO.

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Abstract: The synthesis of a sterically tailored ligand array $(M)_2[(C_5H_2\text{-}2\text{-}Si(CH_3)_3\text{-}4\text{-}C(CH_3)_3)_2Si(CH_3)_2]$ ("M_2Bp") (M = Li, **16**; K, **19**) is described. Transmetallation of Li_2Bp with $YCl_3(THF)_3$ affords exclusively the C_2 symmetric product *rac*-$[BpY(\mu_2\text{-}Cl)_2Li(THF)_2]$, **20**. A X-ray crystal structure of **20** has been determined; triclinic, $P\bar{1}$, *a* = 13.110 (8), *b* = 17.163 (15), *c* = 20.623 (14) Å, α = 104.02 (7), β = 99.38 (5), γ = 100.24 (6)°, Z = 4, R = 0.056. Transmetallation of K_2Bp with $YCl_3(THF)_3$ affords the halide free complex *rac*-BpYCl, **23**. The corresponding *rac*-BpLaCl, **28**, is prepared in an anlogous manner. In all cases the achiral meso isomer is not obtained since only for the racemic isomers are the unfavorable steric interactions between the $Si(CH_3)_3$ groups in the narrow portion of the [Cp-M'-Cp] wedge avoided. Alkylation of **20** or **23** with $LiCH(Si(CH_3)_3)_2$ affords *rac*-$BpYCH(Si(CH_3)_3)_2$, **26** in good yield. Alkylation of **28** with $LiCH(Si(CH_3)_3)_2$ affords *rac*-$BpLaCH(Si(CH_3)_3)_2$, **29.** Hydrogenation of **26** cleanly affords the bridging hydride species $[BpY(\mu_2\text{-}H)]_2$, **27**, as the homochiral (*R,R*) and (*S,S*) dimeric pairs. **26** is an efficient initiator for the polymerization of ethylene to high molecular weight linear polyethylene. **27** catalyzes the polymerization of propylene (25% v/v in methylcyclohexane) and neat samples of 1-butene, 1-pentene, 1-hexene to moderately high molecular weight polymers: polypropylene (M_n = 4,200, PDI 2.32, T_m 157 °C); poly-1-butene (M_n = 8,500, PDI 3.44, T_m 105 °C); poly-1-pentene (M_n = 20,000, PDI 1.99, T_m 73 °C); poly-1-hexene (M_n = 24,000, PDI 1.75, T_m < 25 °C). ^{13}C NMR spectra at the pentad analysis level indicates that the degree of isotacticity is 99% mmmm for all polymer samples. 27 is the first single component *iso-specific* α-olefin polymerization catalyst. The presumed origins of the high isospecificity are presented.

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Chapter 1

Discovery and Development of Ziegler-Natta Catalysis, An Introduction

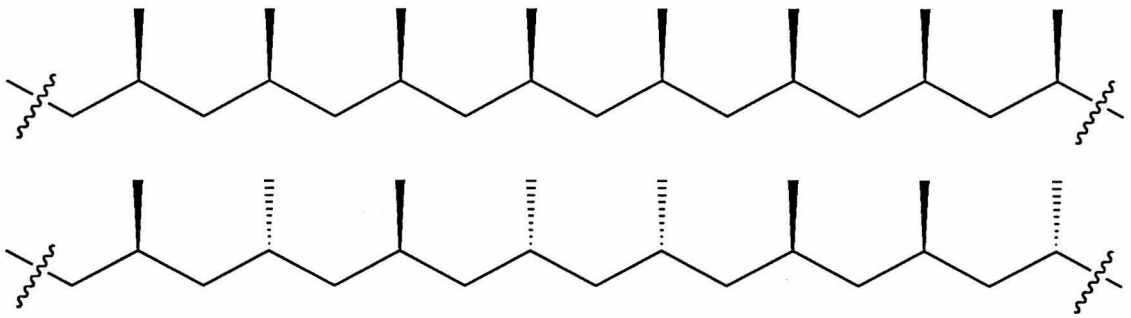
Abstract: A brief introduction to developments in both heterogeneous and homogeneous Ziegler-Natta catalysis is presented to provide context for the experiments performed in Chapters 2 and 3.

Introduction

The transition metal-catalyzed polymerization of ethylene and propylene, now a multi-billion dollar industry was discovered fortuitously nearly four decades ago.[1] During their investigations of ethylene oligomerization using alkyl aluminum catalysts at elevated temperatures (the "Aufbau Reaction"), Ziegler and co-workers discovered that residual colloidal nickel in the reactor greatly facilitated the reaction. Subsequent investigations of other transition metal complexes revealed that various zirconium and titanium salts were exceedingly efficient catalysts. The production of large quantities of linear high molecular weight polyethylene at room temperature and atmospheric pressure was now possible.[2]

Shortly thereafter, Natta and co-workers extended this process to the polymerization of propylene.[3] The catalyst system of $TiCl_4/Al(CH_2CH_3)_3$ was found to polymerize propylene into a heterogeneous material that could be fractionated into several components using different solvents. An oily acetone-soluble fraction, a rubber-like material that was soluble in diethyl ether, and a solid that was soluble in boiling heptane were isolated by successive extraction. Most importantly, there remained a white solid that was insoluble in boiling heptane. This new material was found to be highly crystalline and high melting (> 160 ^oC). Using a variety of techniques (IR spectroscopy, X-ray diffraction) the structures of the polypropylene was assigned that shown in Figure 1. The true three-dimensional structure of the resultant insoluble polypropylene is a 3_1 helical conformation with head-to-tail connectivity of the monomer repeat units. A remarkable feature of the polypropylene produced was the high degree of isospecificity, nearly every tertiary carbon center has the same relative configuration; such an arrangement is termed isotactic. The soluble polymer fractions contain mostly amorphous polypropylene in which there is random orientation of the pendant methyl groups, this configuration is termed atactic.

Figure 1. The structures of isotactic (top), and atactic (bottom) polypropylene.



Until these two discoveries high molecular weight samples of polyethylene and polypropylene were virtually unattainable by conventional polymer synthetic routes (e.g. free radical or cationic polymerization). For their contributions to the chemistry and technology of high polymers Ziegler and Natta were jointly awarded the Nobel Prize in Chemistry in 1963. Following these initial discoveries tremendous effort has been expended towards the development of new catalysts to achieve higher activities and greater control over the physical characteristics of the final polymers.

Several different methods have been developed for determining the relative degree of polymer isotacticity. For polypropylene the percent of the polymer that is not soluble in boiling heptane was taken as a measure of the index of isotacticity. This method is generally only applicable to polymer samples of similar molecular weight, as polymers with either high or low molecular weights can give spurious results. A second method for determining polypropylene stereoregularity is infrared spectroscopy. A reference band (974 cm^{-1}) is found to be independent of the degree of isotacticity. A second band (995 cm^{-1}) has been assigned to absorption by isotactic helices. The ratio of these two absorptions is taken as the isotactic index of the sample.[4] The current state of art for the determination of isotacticity relies on the use of ^{13}C NMR spectroscopy. Details of these analyses are presented in Chapter 3.

The first generation of heterogeneous catalysts were generally preformed solids that contained titanium halides in lower valence states and aluminum alkyls. Four different crystalline forms of $TiCl_3$ exist, and each possesses unique reactivity when subjected to polymerization conditions.[1d] The α form is generated by reduction of $TiCl_4$ with aluminum in a hydrocarbon solvent at 250 °C. The $AlCl_3$ produced co-crystallizes with the $TiCl_3$ to afford α-$TiCl_3 \cdot 0.33AlCl_3$. Reduction at lower temperature, or with H_2 gives β-$TiCl_3$. Heating β-$TiCl_3$ to 150-200 °C produces γ-$TiCl_3$. The δ form exhibits the greatest polymerization activity and can be obtained by prolonged grinding of either α– or γ-$TiCl_3$. The β-form is found to produce amorphous polypropylene. The activity and stereospecificity of the catalyst mixtures is also dependent on the alkyl aluminum co-catalysts. These first generation catalyst systems yielded only moderate amounts of polypropylene, activities of ~20 g polypropylene/(g Ti). Commercialization of this process would have been unfeasible, not only because of the low yield of polymer produced, but also due to the required separation of the crystalline and amorphous polypropylene fractions. Therefore, increased catalytic activity and improved control over polymer morphology were sought.

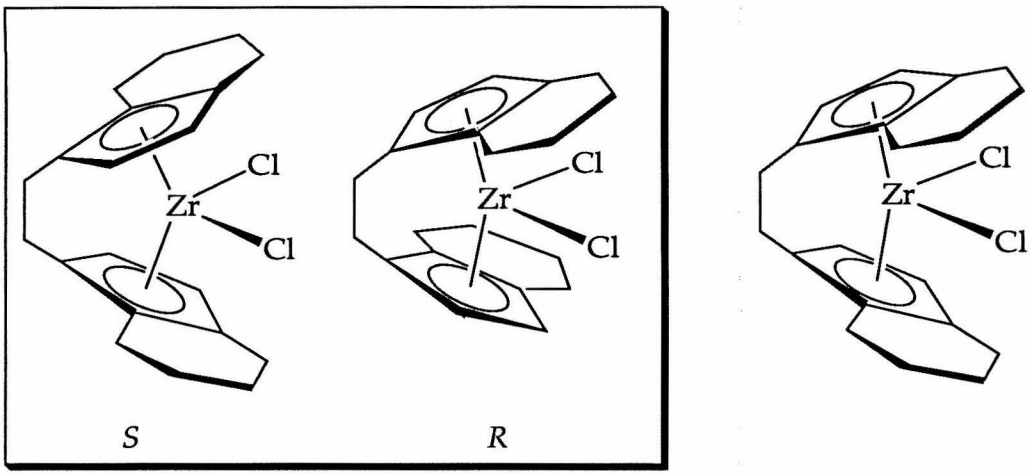
Increased activities were achieved upon addition of Lewis basic donor ligands to the Ti(III) chloride. These second generation catalysts were prepared by milling δ-$TiCl_3 \cdot 0.33AlCl_3$ with donors such as ethers, esters, ketones, amines and amides to produce active catalysts with increased specificities. The role(s) of the donors, however, remains to be elucidated. It is thought that the donors may either form complexes with various active centers and thereby render them chiral, or more stable. Donors may also serve to selectively poison the more active and supposedly less selective centers. Interactions between the Lewis basic donors and the various aluminum centers in the catalyst mixture may also be important. In several of these systems only a small fraction (< 1%) of the titanium present in the catalyst is active.[5] The improved activities achieve polymer production of ~500 g polypropylene/(g Ti), and polymer isotacticities of >90%.

The discovery that dispersion of titanium chloride on certain high surface area supports resulted in increased activities lead to the third generation of Ziegler-Natta catalysts. SiO_2 or Al_2O_3 were useful as supports for ethylene polymerization catalysts; however, these supported transition metal catalysts are not useful for propylene polymerization. Magnesium alkoxides, magnesium dialkyls or activated $MgCl_2$ as supports provide highly active catalysts for the polymerization of ethylene. These supported catalysts are generally produced by ball milling $MgCl_2$ in the presence of ethylbenzoate to form small crystallites; ethylbenzoate is added to the $MgCl_2$ to coordinate surface-exposed Mg centers and thus prevent reaggregation. $TiCl_4$ is next introduced, either neat or in solution, presumably displacing ethylbenzoate from certain sites. Activation with trialkyl aluminum compounds results in an ethylene polymerization catalyst. In order to catalyze propylene polymerization additional electron donors are required. Esters and various amines are found to give highly active and stereospecific catalysts. Once again, the exact role of the donor is unknown. Activities in the range of $5x10^4$ g polypropylene/(g Ti) have been reported with high isotacticities of the resultant polymers being observed as well. A new high mileage catalyst systems has been described by Shell.[6] This so called "super high activity catalyst" uses a $MgCl_2$ support and is reported to have only one type of active center and require only small amounts of alkyl aluminum co-catalysts. Excellent isotacticities and activities as high as $2x10^6$ g polypropylene/(g Ti) are reported.

While there has been tremendous success in developing heterogeneous Ziegler-Natta catalysis for the efficient production of polyethylene and stereoregular polypropylene the nature of these heterogeneous catalyst systems makes them ill-suited for detailed mechanistic study. The exact number and coordination environment about each active center remain unknown. The inclusion of electron donors to modify reactivity further confounds the issue. Parallel investigations into homogeneous Ziegler-Natta catalyst systems have by virtue of their relative simplicity proved more amenable to mechanistic investigation.

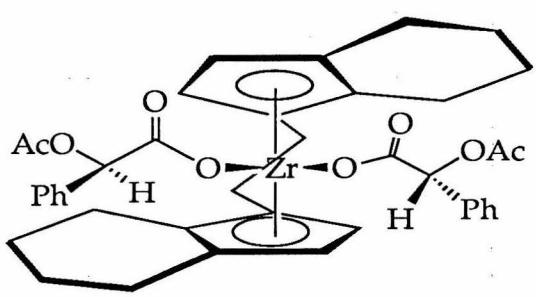
Shortly after the initial discoveries by Ziegler and Natta solutions of titanocene dichloride and alkyl aluminums were reported to be effective catalyst mixtures for the polymerization of ethylene.[7] A major development in the field of homogeneous catalysis was the observation that small amounts of added water, previously thought of as a poison, when added to active catalyst mixtures actually gave *increased* activity.[8] This fact eventually lead to the discovery by Sinn and Kaminsky that treatment of trimethyl aluminum with one equivalent of water results in a rather ill defined methylalumoxane (MAO) comprised of -Al(O)(CH_3)- subunits that in combination with various metallocene dichlorides gave active catalysts.[9] The exact nature of the resultant MAO is unknown, as a variety of linear and cyclic oligomers are present in solution.[10]

An outstanding achievement that greatly advanced homogeneous Ziegler-Natta catalysis was the discovery by Brintzinger and co-workers that the C_2 symmetric *rac*-[ethylenebis-(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, **A**, in conjunction with MAO produced polypropylene with activities and isospecificities that rival some of the very best heterogeneous catalysts.[11] Unfortunately, the large amount of MAO required, 500-1000 fold excess of aluminum to zirconium, in order to achieve activity has made detailed mechanistic investigations into the nature of the active sites exceedingly difficult.

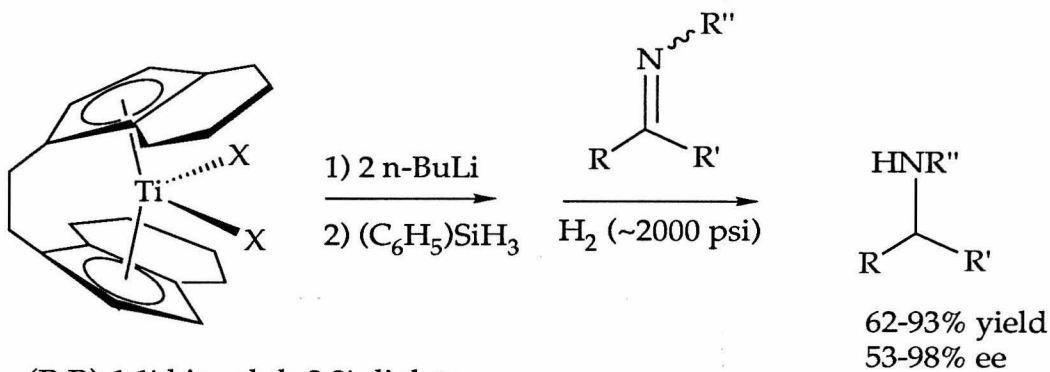


racemic **A** meso **B**

The ability of the **A**/MAO derived catalyst system to polymerize propylene to highly isotactic polypropylene indicates that this ligand ensemble is exceedingly efficient at selecting between the two enantiofaces of propylene for insertion across the metal-carbon bond of the growing chain. Enantiofacial discrimination is a key requisite not only for stereoregular α-olefin polymerization, but also for several transformations in organic synthesis. Resolution of the enantiomers of **A** has proven possible utilizing derivatization with two equivalents of O-acetyl-*R*-mandelic acid to afford diastereomers that are easily separated by crystallization.[12] Alternatively, using 0.5 equivalent of optically pure binaphthol affords the corresponding binaphtholate complexes in which the metal-ligand chirality matches the antipode of binaphthol chosen as an optically enriched diastereomer. Recrystallization once again affords optically pure binaphtholates.[13]



Both stoichiometric and catalytic transformations in organic synthesis have recently been described using **A** or similar derivatives.[14] Use of an optically pure titanium derivative was demonstrated to be an efficient catalyst for the asymmetric hydrogenation of imines to afford chiral amines with moderate to excellent enantiomeric excesses.[15]



62-93% yield
53-98% ee

X_2 = (R,R)-1,1'-binaphth-2,2'-diolate

A persistent drawback to most of the metallocene syntheses described to date has been the co-production of the achiral C_S symmetric meso geometric isomer, **B**. While it is often possible to separate the racemic from the meso isomer by either column chromatography or repeated recrystallizations, the overall yield of the desired racemic isomers generally suffers.

The work of Jordan[16] Bochmann[17] and Teuben[18] on well characterized group IV metallocene alkyl cations has illuminated much about the nature of the active center in metallocene polymerization catalysts. The discrete 14 electron alkyl cations are found to undergo olefin insertion as well as β-H and β-methyl eliminations which model chain propagation and termination steps in Ziegler-Natta catalysis. However, these alkyl cations are generally isolated as Lewis base stabilized cations, and in this form do not polymerize propylene.

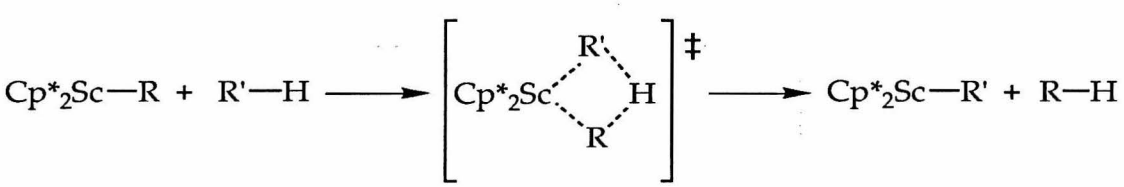
Recent attempts to generate base-free 14 electron metallocene alkyl cations has focused on devising methods to remove a methyl anion from $Cp_2Zr(CH_3)_2$. Several approaches have proved highly successful. The first relies on protonation of $Cp_2Zr(CH_3)_2$ using dimethylanilinium,

$[C_6H_5N(CH_3)_2H]^+$, to remove the methyl anion as methane.[19] A second approach uses the trityl cation, $[(C_6H_5)_3C]^+$, to abstract a methyl anion.[20] In both cases the use of the non-nucleophilic perfluorotetraarylborate counter ion, $[B(C_6F_5)_4]^-$, is chosen to prevent ion pairing, and suppress undesired side reactions. Generation of the 14 electron alkyl cation, $[Cp_2ZrCH_3]^+$ in non-coordinating solvents leads to a catalyst that is capable of polymerizing propylene. An alternative strategy for generating the zirconocene cation utilizes the highly Lewis acidic $B(C_6F_5)_3$ to abstract the methyl anion generating $[Cp_2ZrCH_3]^+[CH_3B(C_6F_5)_3]^-$.[21]

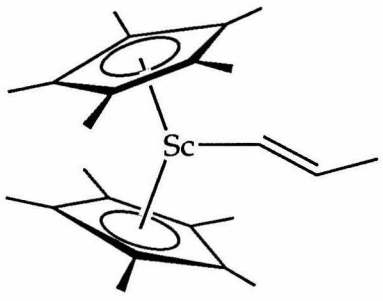
Investigation of isoelectronic yet neutral d^0 group III and d^0f^n lanthanide metallocenes have shown these metallocene alkyl species to be single component catalysts for the polymerization of ethylene.[22] Insertion of α-olefins and elimination sequences, both β-H and β-CH_3, have been studied as models of olefin polymerization and termination steps. However, these 14 electron alkyl complexes are found to produce only oligomers of propylene and higher α-olefins.

Previous work in the Bercaw group has focused on the reactivity of a series of scandocene and related derivative with alkanes and olefins. Initial investigations of permethylscandocene alkyl complexes (Cp^*_2ScR) demonstrated the activation of C-H bonds by a concerted four center process termed σ bond metathesis, Figure 2.[23]

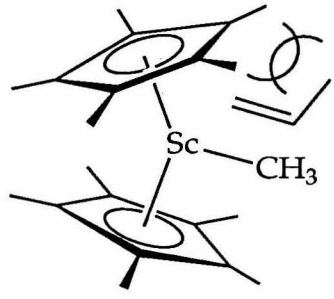
Figure 2. Alkane σ bond metathesis.



At low temperatures permethylscandocenemethyl was found to catalyze the oligomerization of ethylene in a living fashion.[24] Propylene does not undergo insertion into Cp^*_2Sc-CH_3; instead σ bond metathesis occurs to give the vinyl species **C** and methane. Insertion is presumably precluded due to unfavorable steric interactions as shown in **D**.

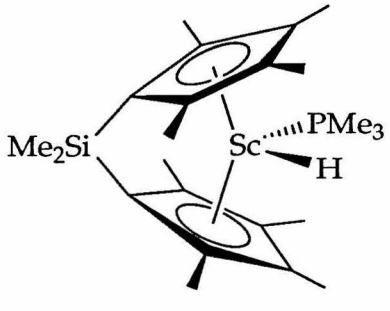


C

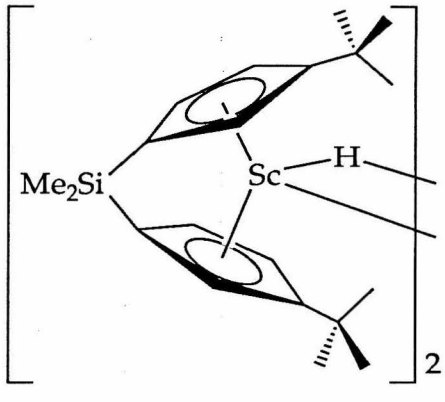


D

A second class of scandocenes utilized [$Si(CH_3)_2$] linked cyclopentadienyl ring systems to afford a more accessible and reactive metal center. The hydride species $(CH_3)_2Si(\eta^5\text{-}C_5(CH_3)_4)_2Sc(H)P(CH_3)_3$ (**E**, OpSc(H)PMe_3) and [*meso*-$(CH_3)_2Si(\eta^5\text{-}C_5H_3\text{-}3\text{-}C(CH_3)_3)ScH]_2$ (**F**, $[DpScH]_2$) were found to selectively dimerize α-olefins in a head-to-tail fashion and to cyclize α-ω-diolefins.[25]

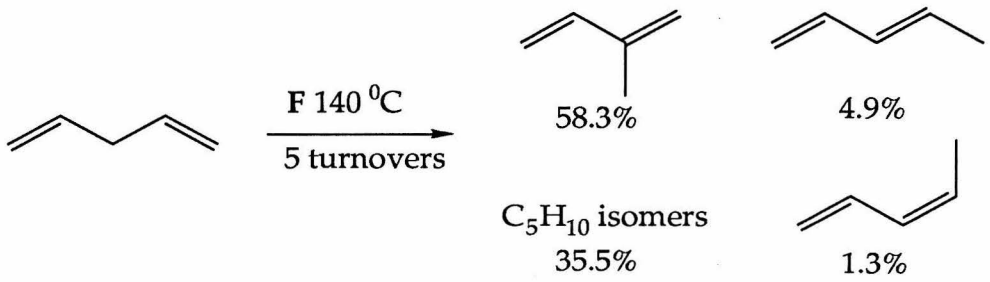


E

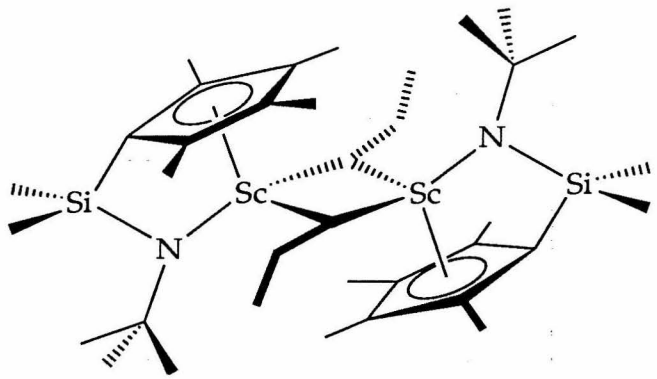


F

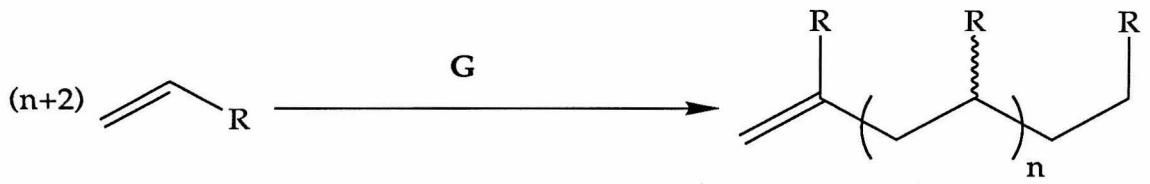
The rate of subsequent monomer additions is slower than the rate of intramolecular β-H elimination, and dimer production dominates. Unusual C-C bond activation was observed for 1,4-pentadienes catalyzed by **F** through a series of reversible olefin insertion and β-alkyl elimination steps.[26]



Modification of the ligand environment about scandium by replacement of a single cyclopentadienyl unit with an alkyl amido fragment was implemented to render the metal center more electron deficient.[27] The increased Lewis acidity of the metal center was expected to result in enhanced reactivity. The synthesis and characterization of a series of scandium complexes based on the dianionic ligand array $[(C_5(CH_3)_4)Si(CH_3)_2(NC(CH_3)_3)]$ ("Cp*SiNR") has been reported.[28] The bridging propyl dimer $[[(\eta^5\text{-}C_5(CH_3)_4)Si(CH_3)_2(\eta^1\text{-}NC(CH_3)_3)]Sc(\mu_2\text{-}CH_2CH_2CH_3)]_2$, **G**, slowly catalyzes the polymerization of propylene, 1-butene, and 1-pentene to moderate molecular weight polymers (M_n 3,000-10,000, versus polystyrene standards, PDI = 1.5-2.1).[29]

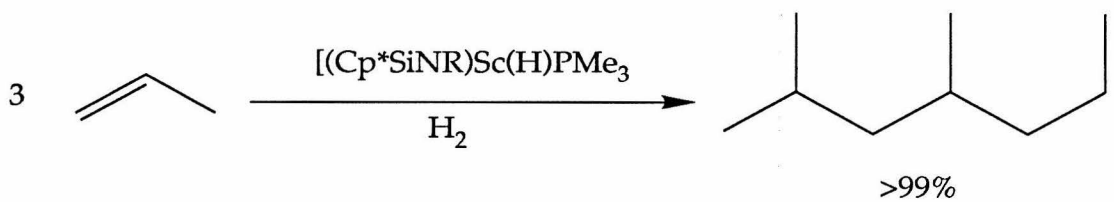


G



R = CH_3; CH_2CH_3; $CH_2CH_2CH_3$

Analysis of the resulting polymer samples by ^1H NMR reveals vinyl endgroups, indicating that chain transfer is occurring predominantly through β-H elimination.[30] The ^{13}C NMR spectra shows the polymers to be essentially atactic.[31] This system is the first well-characterized single component α-olefin polymerization catalyst. Results of H_2 terminated oligomerization studies indicate that the alkanes produced derive mainly (>99%) from head-to-tail coupling.



The relatively simple nature of this catalyst system permitted a detailed mechanistic investigation of olefin insertion into an actual polymerizing chain.[32]

Two proposals for the mechanism of olefin polymerization have been suggested. Cossee and Arlman proposed that there is direct insertion of the olefin across the metal carbon bond, Figure 3.[33] A second proposal offered by Green and Rooney noted that titanium has a variety of accessible oxidation states, and olefin polymerization could occur by an α-elimination, 2+2 cyclization and reductive elimination sequence, Figure 4.[34]

Figure 3. Cossee Arlman direct olefin insertion mechanism.

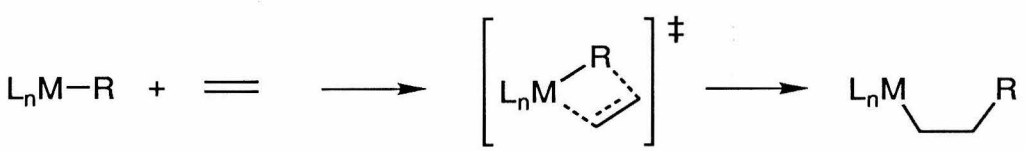
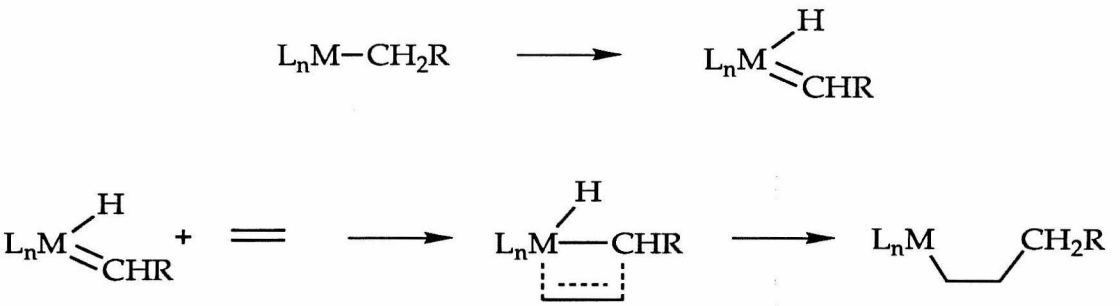
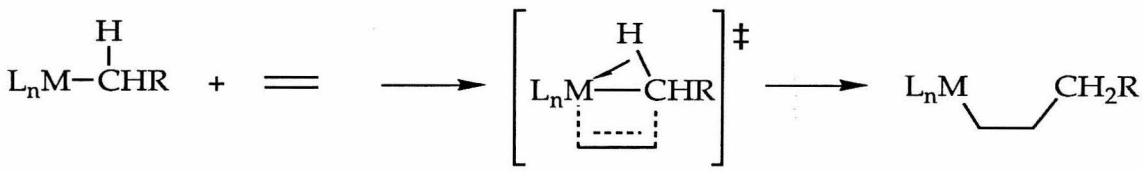


Figure 4. Green Rooney polymerization sequence.



The polymerization activity of the d^0 cationic zirconocene alkyls and the isoelectronic group III and lanthanide metallocenes (vide supra) rules out the possibility of the Green Rooney mechanism as these complexes are unable to undergo the formal 2 electron oxidation required for α-elimination. A modification of this mechanism was subsequently proposed by Brookhart and Green in which an α-agostic interaction serves to facilitate olefin insertion across the metal-carbon bond, Figure 5.[35]

Figure 5. Modification of the Green-Rooney mechanism.



Grubbs and co-workers designed a series of experiments to probe for an α-agostic interaction in the transition state of an intramolecular olefin insertion.[36] Subsequent examinations indicated no isotopic perturbation of the stereochemistry of the products obtained, suggesting no α-agostic assistance for olefin insertion in their system. Recently, however, Bercaw and Brintzinger have reported isotopic perturbations in catalytic transformations on labeled substrates suggesting a M-CH α-agostic interaction being involved in C-C bond formation.[37]

Given the ability of certain metallocene complexes to serve as catalysts for the polymerization of α-olefins to polymers of differing regularity and physical properties it is no wonder that this field of research continues to

receive considerable attention in both academic and industrial laboratories.[38] The emergence of metallocenes in both catalytic and stoichiometric transformations in organic synthesis will certainly promote further investigations into the development and exploration of new metallocenes. The astounding iso-specificities of polymers produced by C_2 symmetric ansa-metallocenes as well as the excellent enantiomeric excesses observed in several transformations performed by optically pure derivatives prompted us to begin investigations into developing new C_2 symmetric metallocenes. Chapter 2 describes the synthesis of a tailored ligand array that was designed with specific steric factors to favor the formation of C_2 symmetric metallocenes, and minimize formation of the meso geometric isomer. These goals have been met with the synthesis and characterization of a series of novel ansa-yttrocene and ansa-lanthocenes.[39]

The multicomponent nature of several homogeneous polymerization catalysts hampers detailed mechanistic investigations, therefore, we sought to develop a single component catalyst system capable of polymerizing α-olefins. Chapter 3 explores the reaction chemistry of several C_2 symmetric 14 electron yttrocene alkyl and hydride derivatives towards α-olefins. Indeed these complexes have been found to be the first single component *iso-specific* α-olefin polymerization catalysts. The outstanding isotacticities of the resulting poly-α-olefins are demonstrated and a hypothesis concerning the origin of the stereoregularity is presented.[40] These initial investigations were focused on studying formation of isotactic poly-α-olefins with the hope being that factors responsible for the isospecificity would not only lead to development of superior polymerization catalysts but also for extension to reagents or catalysts for enantioselective transformations in organic synthesis.

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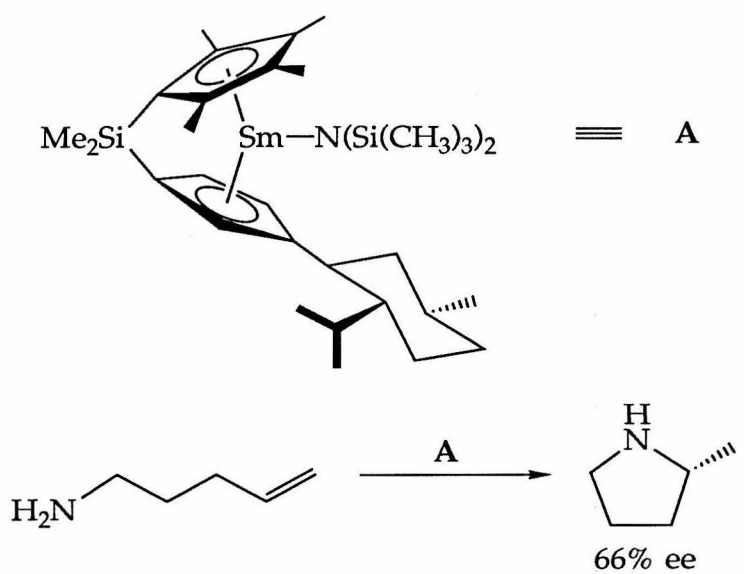
Chapter 2

Design of a Sterically Tailored Bridged Dicyclopentadienyl Ligand Array. Synthesis and Characterization of C_2 Symmetric ansa-Yttrocene and ansa-Lanthanocenes

Abstract: The synthesis of a sterically tailored ligand array is described. Silylation of $Li_2[(C_5H_2\text{-}3\text{-}C(CH_3)_3)_2Si(CH_3)_2]$ with 2 equivalents of $ClSi(CH_3)_3$ followed by double deprotonation affords the tailored ligand salt $M_2[C_5H_3\text{-}2\text{-}Si(CH_3)_3\text{-}4\text{-}C(CH_3)_3]_2Si(CH_3)_2]$ (M = Li, **16**, M = K, **19**) in moderate to excellent yield. Transmetallation with group III metal chlorides affords exclusively *rac*-$[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2MCl]$ (M = Y, **23**, M = La , **28**). The achiral meso isomers are not obtained since only for the racemic isomers are the unfavorable steric interactions between the $Si(CH_3)_3$ groups in the narrow portion of the [Cp-M-Cp] wedge avoided. The alkyl complex **26** is obtained by treatment of **23** with $LiCH(Si(CH_3)_3)_2$. Hydrogenation of **26** results in a dimeric hydride species
[*rac*-$(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2M(\mu_2\text{-}H)]_2$, **27**.

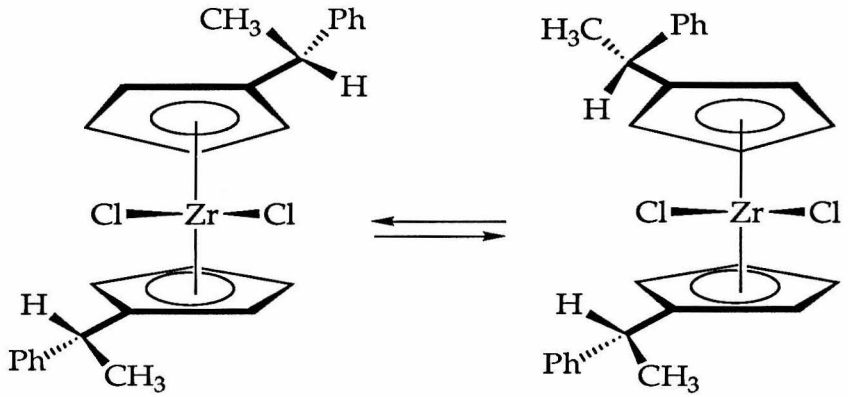
Introduction

The cyclopentadienide anion has become one of the most versatile ligands in organometallic chemistry. Complexes of this ligand with all d-block and several f-block metals are known. Use of a single cyclopentadienyl results in a piano stool complex, $CpML_n$, use of a second cylcopentadienyl gives the familiar metallocenes, Cp_2ML_n. Cyclopentadienyl transition metal and metallocene complexes are known to serve as useful reagents, both in stoichiometric and catalytic fashions, for a wide variety of reactions.[1] Chiral analogs offer the possibility for performing enantioselective transformations.[2] Attachment of a single chiral substituent to a cyclopentadienyl ring will result in a chiral C_1 symmetric metallocene. Marks and co-workers have synthesized a series of chiral lanthanide metallocenes, utilizing menthyl and neomenthyl substituents. These particular substituents are chosen such that diastereomeric formation during the synthesis allows for resolution to optically pure complexes, i.e. **A**. These complexes have demonstrated their utility in catalyzing the hydroamination-cyclization of aminoolefins.[3]



Erker and co-workers have adopted a similar strategy in employing at least one chiral substituent on each cyclopentadienyl ring.[4] The steric

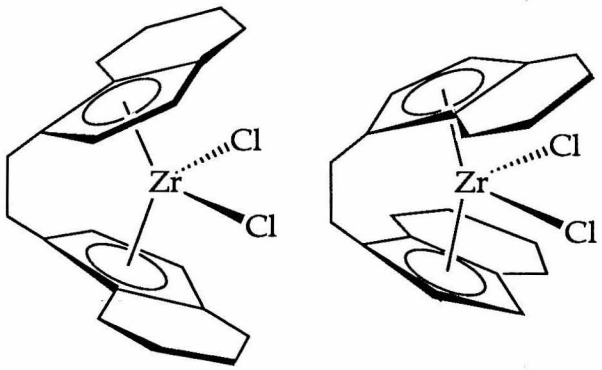
influence exerted by the chiral substituents is, however, lessened by free rotation of the cyclopentadienyl ring about the metal-centroid axis.



C_2 Symmetric C_S symmetric

Dynamic NMR studies have shown there to be rapid interconversion between the C_2 and C_S symmetric forms in solution. This class of metallocenes in conjunction with MAO is found to polymerize propylene to give polypropylene with both crystalline and amorphous blocks. This class of materials may find eventual use as thermoplastic elastomers. However, the multiple conformers present makes these metallocenes poorly suited for performing enantiospecific transformations.

Arresting the cyclopentadienyl rotation can be accomplished by the use of an interannular bridge to link the two cylopentadienyl rings, resulting in the so-called ansa-metallocenes.[5] This linkage does not in itself guarantee a C_2 symmetric metallocene. It was not until 1982 that a report by Brintzinger and co-workers demonstrated that chiral, by virtue of their C_2 symmetry, ansa-metallocenes could be synthesized using judicious placement of substituents on the cyclopentadienyl rings.[6]

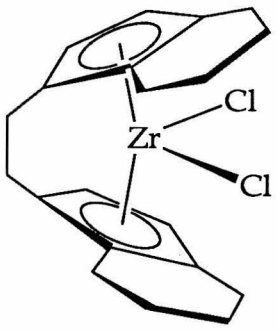


S *R*

racemic

Following the pioneering work of Brintzinger there has been tremendous effort devoted by several workers toward the synthesis of C_2 symmetric ansa-metallocenes. Early transition metal C_2 symmetric metallocenes have received considerable attention as catalysts for the polymerization of ethylene and, more importantly, for the conversion of α-olefins to high molecular weight isotactic polymers.[7] Recently, these metallocenes have seen increased utility in both catalytic and stoichiometric transformations in organic synthesis.[8]

One rather severe drawback in the synthesis of C_2 symmetric ansa-metallocenes from the reaction of the linked dicyclopentadienide dianion and transition metal halide is the co-production of the achiral meso geometric isomer which possesses an internal mirror plane relating the two cyclopentadienyl rings, C_S symmetric.

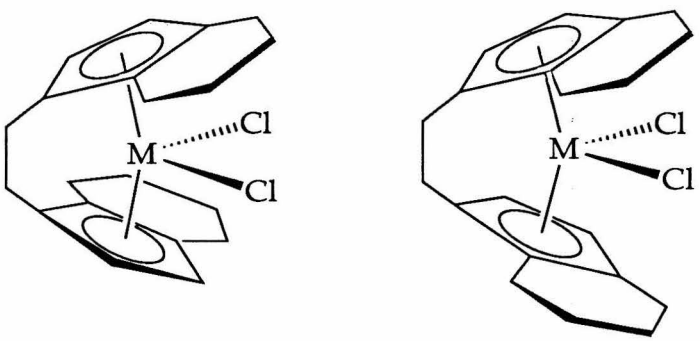


meso

Assuming that the synthesis of these metallocenes proceeds in a stepwise fashion, it is clear that the attachment of the second cyclopentadienyl ring will determine the stereochemistry of the final product, either racemic (C_2 symmetric) or meso (C_S symmetric). While there has been a suggestion as to the mechanism of cyclopentadienide attachment to transition metal halides there remains much ambiguity as to the exact mode of pentahapto bond formation.[9] Based on these hypotheses the reaction can be directed towards formation of either geometric product by influencing the mode of the second cyclopentadienyl ring attachment. Moreover, if a method were devised towards exclusive formation of the racemic isomers then factors that govern the first cyclopentadienyl ring attachment could be explored with the hope of eventually leading to stereoselective ansa-metallocene syntheses.

In the syntheses of ansa-metallocenes, the two most prevalent choices for the interannular bridge are either a two carbon ethano (C_2H_4) linkage or the single atom dimethylsilyl ($(CH_3)_2Si$) linker. These are chosen for their relative ease in synthetic introduction starting from either 1,2-dibromoethane or dichlorodimethylsilane and two equivalents of the appropriate cyclopentadienide anion. In general, the single atom linker provides for a more rigid ansa-metallocene framework as evidenced by the formation of two crystallographically independent forms of several ethano bridged ansa-metallocenes.[10] The deviations from C_2 symmetry observed in the solid state are not apparent in solution as NMR spectroscopy indicates unrestricted fluctuation between the two conformations.

To date there have been numerous preparations of group IV ansa-metallocenes generally starting from the alkali metal salt of the tethered ligand and the appropriate metal chloride. One of the most widely investigated ansa-metallocene is the aforementioned ethylenebis-(4,5,6,7-tetrahydro-1-indenyl)metal dichloride ((EBTHI)MCl_2) **1**. Indeed, the first example of a homogeneous isospecific polymerization of propylene was performed with this ligand array.[11] The enantiomers of this system can be resolved utilizing O-acetyl-*R*-mandelic acid diastereomeric derivatization followed by crystallization.[12] Optically pure derivatives of **1** have been used successfully for the catalytic asymmetric hydrogenation of imines, and the catalytic reduction of esters to alcohols.[8]



racemic *meso*

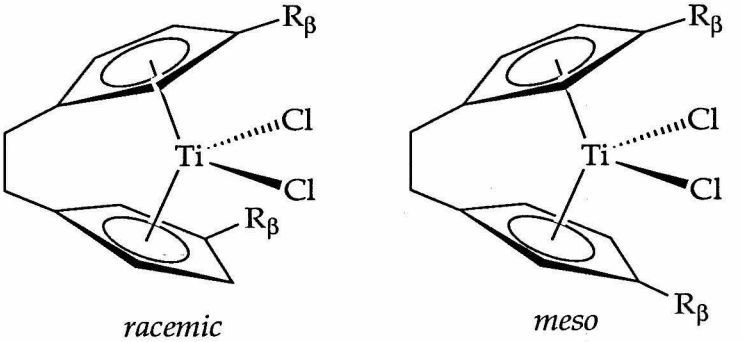
1

a: M=Ti, b: M=Zr, c: M=Hf

In practice, the synthesis of the precursor ethylenebis(indenyl)metal dichloride usually proceeds with a rather poor racemic/meso ratio, varying between 1 to 2 and 1 to 10. The racemic isomers are the thermodynamically preferred products with greater amounts being formed under higher reaction temperatures. The tetrahydro derivative is obtained by selective PtO_2 catalyzed hydrogenation of the exo face of the ethylenebis(indenyl)metal dichloride in order to afford more tractable complexes.[13] In the case of titanium the geometric isomerization of the ansa-metallocene from the meso to racemic forms is conveniently carried out by photolysis. The racemic isomers are less soluble in a variety of solvents with the result being that pure **rac-1a** can be obtained as a crystalline solid directly from the photolysis. Presumably, the mechanism of isomerization involves homolytic cleavage of

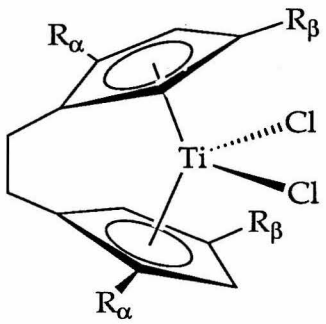
the metal cyclopentadienyl bond as has been reported for other titanocene derivatives.[14] The preparation of the zirconocene derivative **rac-1b** is fortuitous in that the racemic isomers preferentially crystallize from the reaction mixture.[15] A revision of the original X-ray crystal structures for the racemic forms of the titanocene and zirconocene dichlorides has been published.[16] The structure of the hafnium complex **rac-1c** has been reported; however, neither synthetic details nor racemic/meso ratio data were given.[17]

A series of mono substituted ethano-linked titanocene dichlorides, **2**, has been reported.[18] Variation of the alkyl substituents at the β-carbon (R_β = CH_3 **a**, CH_2CH_3 **b**, $CH(CH_3)_2$ **c**, $C(CH_3)_3$ **d**) resulted in little change in the racemic/meso ratios ranging between 1:1.3 and 1:2. However, in at least one case, **2d** (R_β = $C(CH_3)_3$), the geometric isomers were separable by column chromatography.

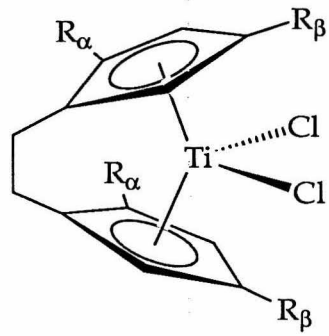


2

In a related series of compounds prepared by these same workers a second set of alkyl substituents located in the proximal position adjacent to the interannular bridge, was found to afford improved racemic/meso ratios, Table I.[19] Once again photolysis enriched the mixtures in the racemic isomers, and pure racemic compounds could be obtain by either crystallization or column chromatography.



racemic



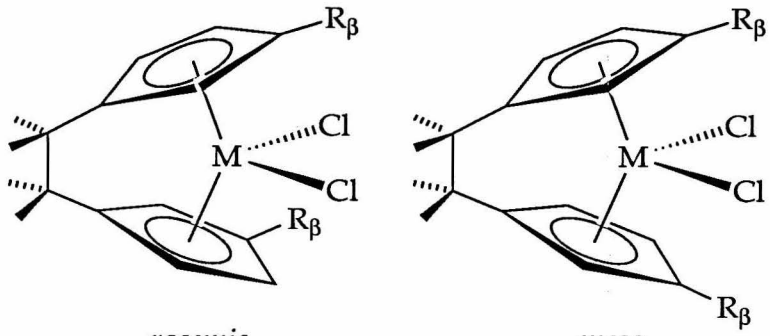
meso

3

Table I. Synthetic and photostationary racemic/meso ratios for **3**.

	Rα	Rβ	Synthetic		Photostationary	
			rac	*meso*	*rac*	*meso*
3a	CH_3	CH_3	2	1	2.5	1
3b	CH_3	$CH(CH_3)_2$	2.6	1	4	1
3c	CH_3	$C(CH_3)_3$	1.6	1	15	1

Use of the more sterically demanding tetramethylethano bridging unit results in moderate selectivities for production of the desired racemic isomers of complexes **4** and **5**, Table II.[20]



racemic *meso*

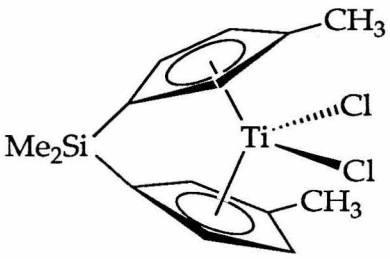
5 M=Ti, 6 M=Zr

Table II. Racemic/meso ratios for **4** and **5**.[a]

	R_b	M	*rac*	*meso*
4a	$C(CH_3)_3$	Ti	2.5	1
4b	$Si(CH_3)_3$	Ti	0.6	1
			1.8	1
4c	$CH(CH_3)_2$	Ti	1	1
4d	$CH_2C_6H_5$	Ti	1	1
4e	$C(CH_3)_2C_6H_5$	Ti	1.2	1
			2.2	1
4f	$C(CH_2)_5C_6H_5$	Ti	1.2	1
			2.2	1
5a	$C(CH_3)_3$	Zr	1.5	1
			2	1
5b	$Si(CH_3)_3$	Zr	1.5	1
			2	1

a) Multiple entries are for two different syntheses.

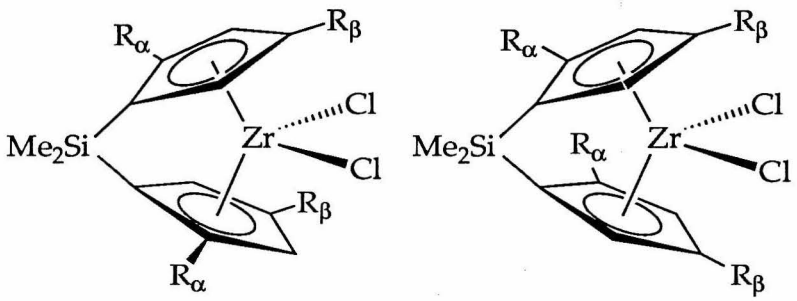
The use of a single atom tether in the case of the dimethylsubstituted ansa-cyclopentadienyl **6** did not produce the racemic isomer as evidenced by the inequivalency of the two methyl groups of the dimethylsilyl linker in the ^1H NMR spectrum. No mention was made to the particular product(s) obtained.[21]



racemic
Not Obtained

6

In the synthesis of the corresponding zirconocenes, **7**, no preference for the production of the racemic isomers over the meso isomer was observed with only one alkyl substituent present on each cyclopentadienly ring, Table III **7a-d**.[22] Nevertheless, bias towards formation of the desired racemic isomers is observed when a methyl group is placed on the cyclopentadienyl in a position proximal to the dimethylsilyl linker, Table III **7e-f**.



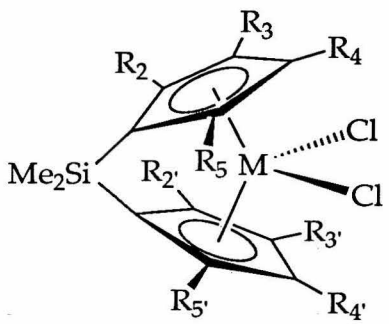
racemic *meso*

7

Table III. Racemic/meso ratios for dimethylsilyl bridged **7**.

	R_α	R_β	*rac*	*meso*
7a	H	$C(CH_3)_3$	1	1
7b	H	$Si(CH_3)_3$	1	1
7c	H	$C(CH_3)_2C_6H_5$	1	1
7d	H	$C(CH_2)_5C_6H_5$	1	1
7e	CH_3	$C(CH_3)_3$	2	1
7f	CH_3	$CH(CH_3)_2$	6	1

An extensive study of the synthesis of several mono-, di- and trisubstituted dimethylsilyl linked zirconocene and hafnocenes reveals once again that the placement of methyl or *tert*-butyl groups on the cyclopentadienyl rings can give moderate improvements in the racemic/meso ratio, Table IV.[23]



8 M=Zr, 9 M=Hf

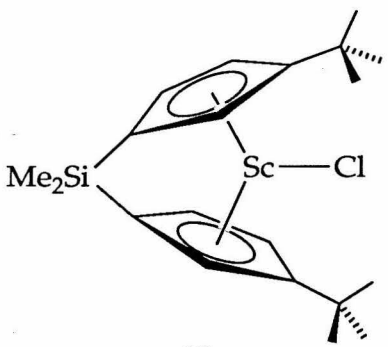
Table IV. Racemic/meso ratios for dimethylsilyl bridged **8** and **9**.

	M	R_2	R_3	R_4	R_5	$R_{2'}$	$R_{3'}$	$R_{4'}$	$R_{5'}$	rac	meso
8a	Zr	CH_3	CH_3	H	CH_3	CH_3	H	CH_3	CH_3	5.6	1
8b	Zr	CH_3	H	CH_3	H	H	CH_3	H	CH_3	15.7	1
8c	Zr	H	$C(CH_3)_3$	H	H	H	H	$C(CH_3)_3$	H	2.7	1
8d	Zr	H	CH_3	H	H	H	H	CH_3	H	7.3	1
9a	Hf	CH_3	CH_3	H	CH_3	CH_3	H	CH_3	CH_3	13.3	1
9b	Hf	CH_3	H	CH_3	H	H	CH_3	H	CH_3	100	1
9c	Hf	H	$C(CH_3)_3$	H	H	H	H	$C(CH_3)_3$	H	1	2.8
9d	Hf	H	CH_3	H	H	H	H	CH_3	H	1.1	1

The improved racemic/meso ratio for the *tert*-butyl ansa-metallocene **8c** in the present study (2.7:1) compared to that reported previously for **7a** by Brintzinger (1:1) certainly reflects the different methods of workup and serves as a reminder that the values reported are not absolute. Nevertheless, they

do provide a good indication as to how efficiently the syntheses of the desired C_2 symmetric ansa-metallocenes can be achieved. In general separation of the racemic isomers from the meso isomer is possible through either repeated recrystallizations or by column chromatography.

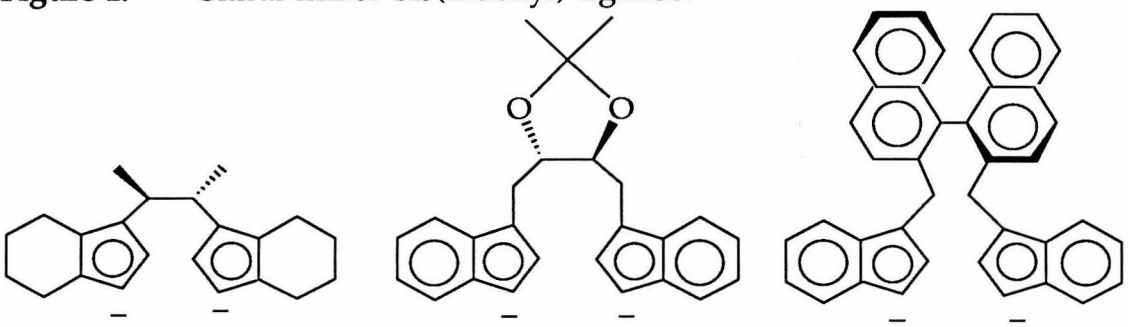
Prior to the work presented in this thesis, the only other attempt to attach a potentially C_2 symmetric ansa-ligand framework to a group III metal had been a report from this group on the synthesis of **10** starting with $Li_2[(CH_3)_2Si(3\text{-}(CH_3)_3C\text{-}C_5H_3)_2]$ and $ScCl_3(THF)_3$.[24] The resulting product, however, was found to be exclusively the C_s symmetric meso isomer.



10

Recently there has been considerable interest in the synthesis and utility of chiral analogs to several of the ansa-metallocenes presented above. The use of an ansa-metallocene with a chiral linker is hoped to preclude the formation of the achiral meso isomer. An additional benefit is the potential of diastereomeric formation such that resolution of the resultant C_2 symmetric ansa-metallocenes might prove possible. Several strategies have emerged based on the bis(indenyl) metallocene motif, Figure 1.

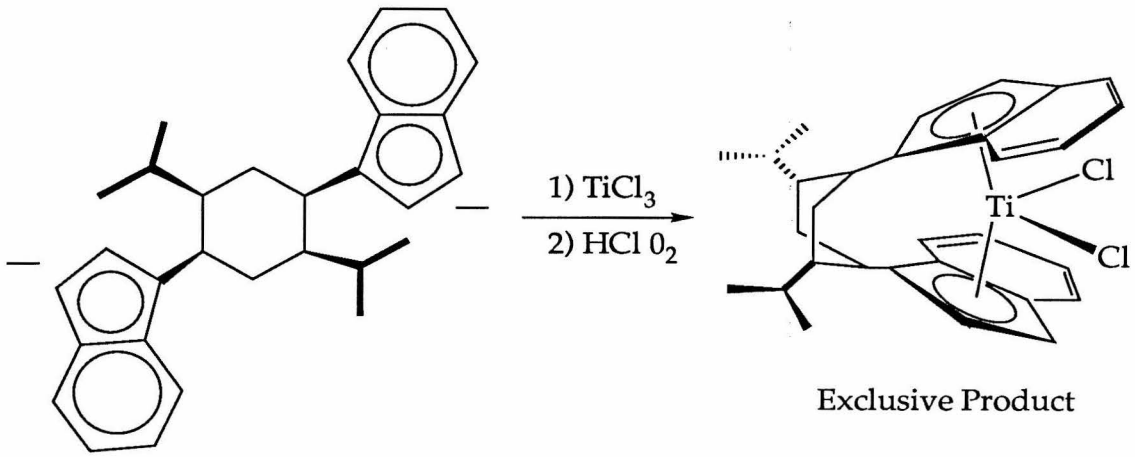
Figure 1. Chiral linker bis(indenyl) ligands.



11 **12** **13**

The chiral dimethylethano bridged ligand **11** was found to give a mixture of isomers for both the titanium and zirconocene complexes. Photochemical interconversion gave a diastereomerically pure titanium derivative; however, the protracted synthesis of the ligand precursor coupled with the low overall yield makes this a poor choice for further study.[25] The acetonide bridged indenyl species, **12**, gave only the meso isomers for the zirconium complex, and presumably also for the titanium derivative.[26] The binaphthyl bridged ligand, **13**, was found to give chiral isomers; however, the solid-state structures for both the titanium and zirconium derivatives reveal that there is significant distortion from the desired C_2 symmetric arrangement due to the large conformational constraints of the linker.[27]

Two other strategies have been developed to enforce diastereomeric formation that have proven more successful. The first utilized a 2,2'-biphenyl linker such that racemization is prevented by the rigidity of the biphenyl. However, the metallation steps were found to proceed in rather low yield (3-18%) following a rather lengthy and only moderately efficient synthesis.[28] A second and more successful approach was the use of a chiral cyclohexane-1,4-diindenyl framework which afforded in high yield a single diastereomer.[29]



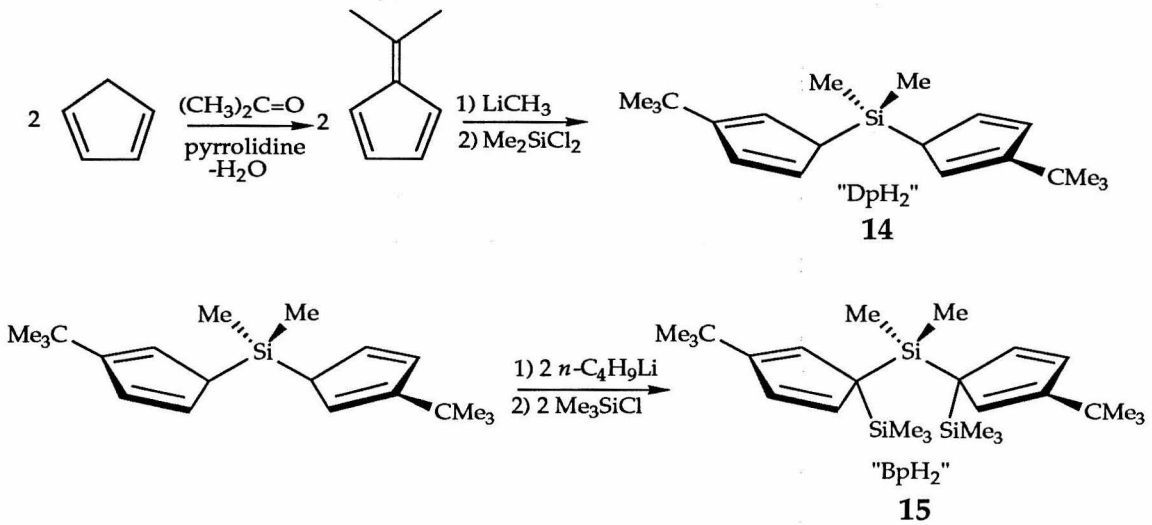
Exclusive Product

With the tremendous success of C_2 symmetric ansa-metallocenes in a wide variety of catalytic and stoichiometric reactions, it is no wonder that the synthesis of new ligands is currently an area of very intense investigation. There are, however, several pitfalls with many of the current ligand designs including little or no control over the resulting racemic to meso ratio as well as lengthy and inefficient syntheses. While it is generally true that separation of the racemic isomers from the meso isomer can be accomplished, only in the case of the titanocene derivatives is the photolytic interconversion possible. Thus the separation by chromatography or selective crystallization may ultimately afford the desired racemic isomers, but this is usually accomplished with further reduction in yield. Realizing the importance of steric substitution at the position proximal to the interannular bridge in favoring the formation of the desired racemic products in ansa-metallocene syntheses, we reasoned that placement of a substituent that was more sterically demanding than a methyl group at the proximal should lead to enhanced racemic to meso ratios. An obvious benefit to this strategy is that an increase in the racemic to meso ratio not only will make the overall synthesis more efficient, but may obviate the need to separate the undesired meso isomer should its formation be completely suppressed. The synthesis of such a ligand array is described and the exclusive formation of C_2 symmetric ansa-yttrocenene and ansa-lanthanocenes is presented.

Results and Discussion

We have found a route into a synthetically tailored ligand precursor, "BpH_2", **15**, which starts with the known $Li_2[(CH_3)_2Si(3\text{-}(CH_3)_3C\text{-}C_5H_3)_2]$ (Li_2Dp) and utilizes silylation of the two cyclopentadienide anions to introduce two sterically demanding $(CH_3)_3Si$ groups. The ligand precursor synthesis is shown in Figure 2.

Figure 2. Synthesis of the ligand precursor **15**.

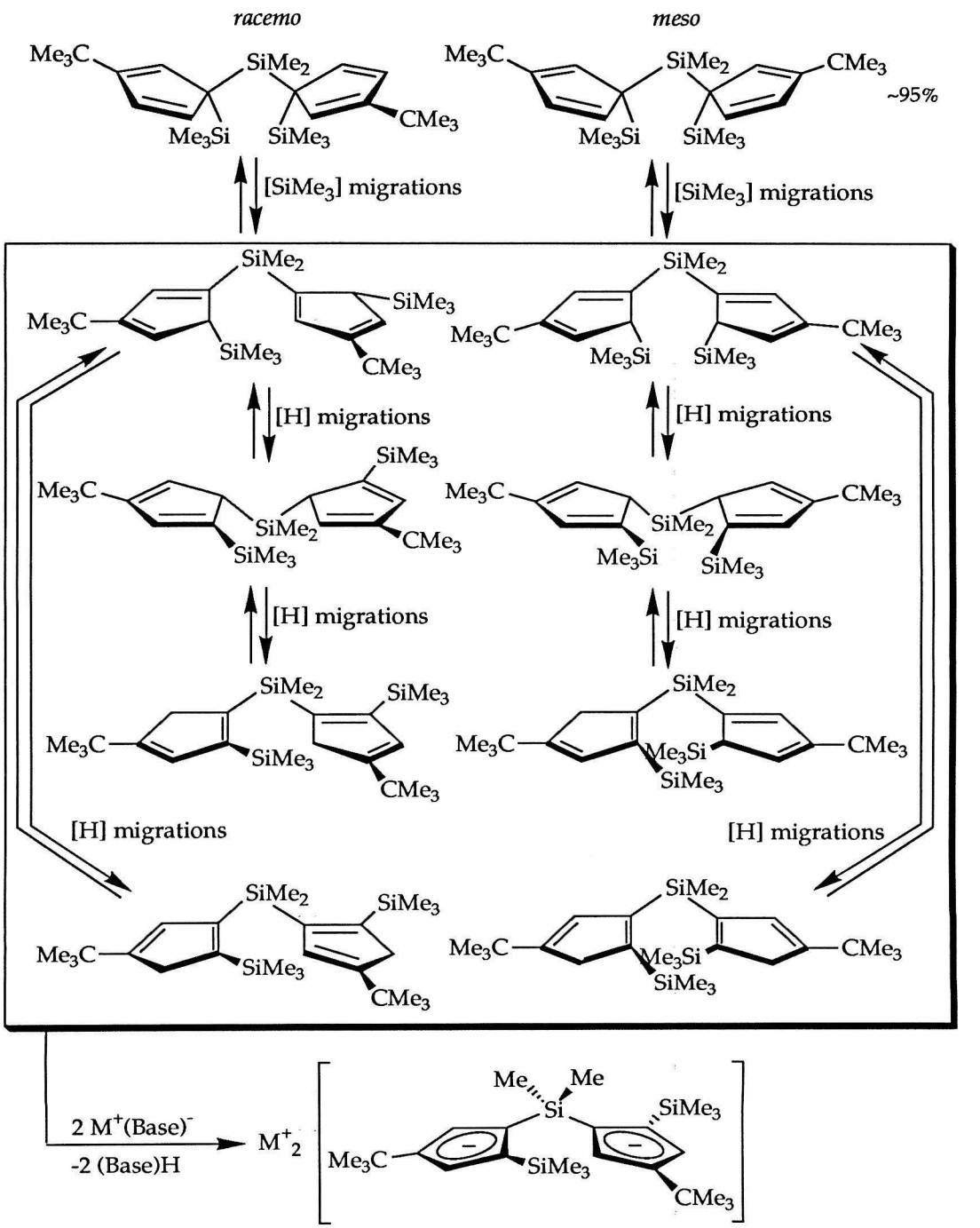


The condensation of cyclopentadiene with acetone is conveniently carried out using only a catalytic amount of pyrrolidine as opposed to a stoichiometric equivalent as reported previously.[30] Addition of methyl lithium to 6,6-dimethylfulvene proceeds in nearly quantitative yield affording $Li[(CH_3)_3C\text{-}C_5H_4]$. Linking two equivalents of $Li[(CH_3)_3C\text{-}C_5H_4]$ with the single atom bridging precursor $(CH_3)_2SiCl_2$ followed by deprotonation with 2 equivalents of n-butyllithium affords $Li_2[(CH_3)_2Si(3\text{-}(CH_3)_3C\text{-}C_5H_3)_2]$ (Li_2Dp) in very good yield (>85%). Subsequent silylation is readily accomplished by addition of a slight excess of $(CH_3)_3SiCl$ to a THF solution of Li_2Dp. Removal of the by-product LiCl followed by shortpath vacuum distillation of the crude product (150 °C, 1μ Hg) affords the ligand precursor

BpH_2, **15**, as a viscous yellow liquid in high yield. After standing for several weeks the liquid solidifies to a low melting yellow solid.

The silylation of **14** to give **15** occurs such that both the trimethylsilyl and the dimethyl linker preferentially reside on the doubly allylic ring carbon.[31] As observed for many other main group substituted cyclopentadiene there exists several low energy H and Si 1,2 sigmatropic shifts.[32] This results in several possible regio- and stereoisomers for **15** such that the ^1H NMR is extremely complex, Figure 3. Subsequent double deprotonation of **15** (vide infra) results in only a single product. This result is not at all unexpected since the steric influence of the tert-butyl group is effectively greater than that of the trimethylsilyl groups due to the shorter C-C versus Si-C bond distances. The steric bulk of the tert-butyl group is held closer to the cyclopentadienyl ring and thus forces the two silyl groups to occupy neighboring positions.[33]

Figure 3. Several of the possible conformation isomers of **15**.



Deprotonation of **15** can be accomplished with a variety of bases. The use of n-butyllithium is not entirely satisfactory due to the extremely high solubility of the resultant Li_2Bp, **16**, in cold hexanes which renders isolation of the final product problematic. Maximum yields of **16** isolated as a white crystalline solid range from 10-25%. The solution behavior of **16** in non-coordinating solvents is intriguing. The ^1H NMR spectrum (C_6D_6) at ambient temperature displays a sharp singlet for the tert-butyl groups, however, the resonances for the trimethylsilyl groups and the dimethylsilyl linker are very broad. Upon warming these two resonances begin to sharpen, indicative of restricted rotation of these two neighboring groups being responsible for the broadened signals.

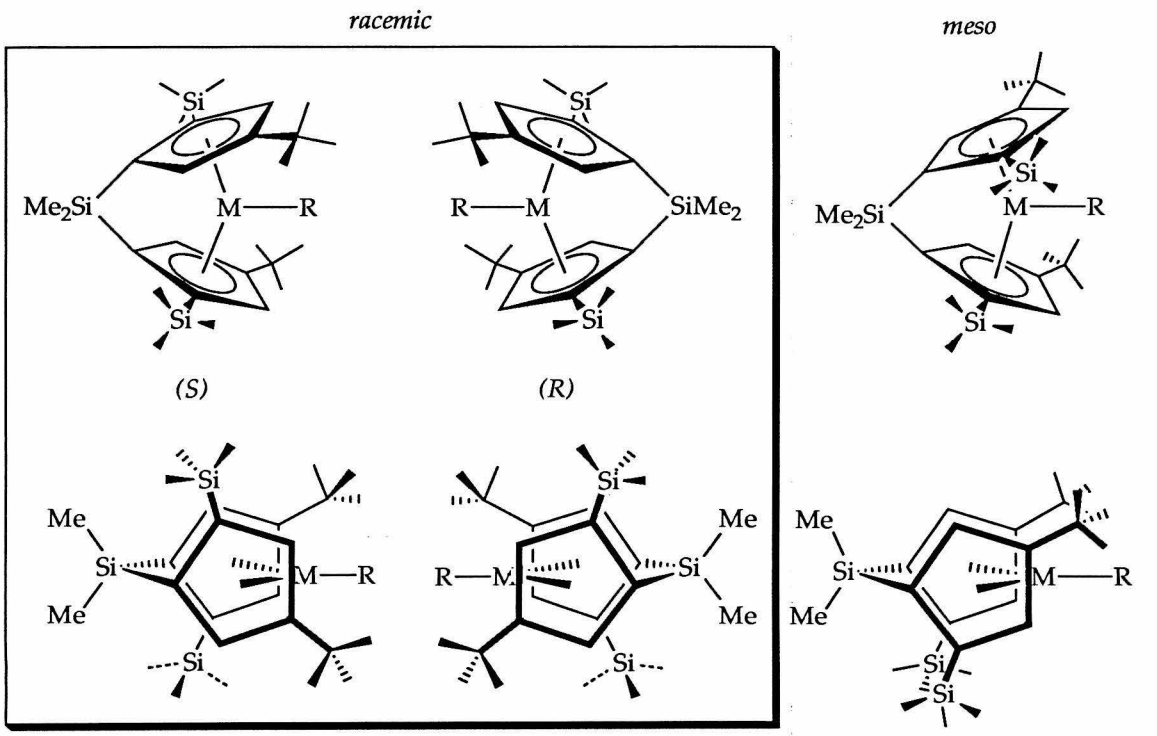
The difficulty in isolating **16** prompted us to find alternative methods for the synthesis of the dilithio ligand salt. The use of the chelating Lewis base tetramethylethylenediamine (TMEDA) in conjunction with n-butyllithium results in immediate deprotonation of **15** and formation of a petroleum ether insoluble white solid which analyzes for ($Li_2(TMEDA)_2Bp$), **17**. When 1,2-dimethoxyethane (DME) is used as the Lewis base concentration of the resulting petroleum ether solution is required followed by cooling to -30 °C in order to eventually isolate a white crystalline solid ($Li_2(DME)_2Bp$), **18**. Unfortunately, both of these complexes proved to be less than ideal due to subsequent difficulties following the transmetallation steps (vide infra).

In an attempt to avoid the commonly encountered problems in removing lithium ions from the product following transmetallation, routes to other alkali metal ligand salts were investigated. Deprotonation of **15** with KO*t*Bu proved generally more satisfactory than using either KH or $KCH_2(C_6H_5)$, as the former has greater solubility in THF. Following deprotonation the resultant white solid was ground to a fine powder and placed under vacuum at 60 °C overnight to ensure complete removal of *tert*-butyl alcohol. Yields are generally quite good to excellent with the added advantage that K_2Bp, **19**, is only moderately soluble in toluene and THF but insoluble in petroleum ether. The overall synthesis of **19** can be

accomplished in six steps starting from cyclopentadiene with each step proceeding in greater than 80% yield.

The stereochemistry of metallocenes has been reviewed by Schlögl.[34] Determination of chirality for ansa-metallocenes is based upon a modification of the Cahn-Ingold-Prelog system. If all bonds from the metal atom are arbitrarily considered as single bonds then asymmetric substitution of a cyclopentadienyl ring causes all of the ring C atoms to become chiral centers. Using the standard Cahn-Ingold-Prelog priority numbering system, the determination of the chirality at the bridgehead carbon will give the relative assignments. The three possible modes of coordination for the sterically tailored Bp ligand to a metal alkyl fragment are shown in Figure 4.

Figure 4. Chiral (boxed) and achiral isomers of BpM-R.



The reaction of **16** with $YCl_3(THF)_3$ proceeds readily in hot (80 °C) toluene over the course of three days. Examination of the crude reaction mixture shows there to be little or no formation of the meso isomer. Apparently, the eclipsed confirmation of the two trimethylsilyl groups in the narrow portion of the bent metallocene for the meso isomer is sufficient to preclude its formation. This results in the exclusive formation of the C_2 symmetric *rac*-$[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]Y(\mu\text{-}Cl)_2Li(C_4H_8O)_2$, **20**, Figure 5.[35]

It should be noted that the retention of LiCl, as in the case of **20**, is a common occurrence in the synthesis of highly Lewis acidic group III and lanthanide metallocenes.[36] An X-ray diffraction study was conducted on a single crystal of ***rac*-20** grown by slow cooling of a petroleum ether solution. A molecular drawing is shown in Figure 6. The full details of this investigation have been reported elsewhere,[37] and thus only selected features will be presented herein. There are virtually two identical molecules for each enantiomer in the asymmetric unit and all discussion of metrical parameters will use an average of the two values obtained. A center of inversion in the unit cell relates the *R* and *S* enantiomers. The centroids of the Cp rings are 2.388[6] Å from the Y atoms, but the Cp planes are not perpendicular to the Y-Cp centroid vectors. The Y-C(Cp ring) distances range from 2.585[5] Å to 2.817[6] Å with the carbon atom attached to the Si linker having the shortest distance. This decrease in Y-C bond distance is also evidenced by a compression of the C-Si-C bond angle to 99.3[3]°. One remarkable feature of the structure that attests to the large steric presence of the $(CH_3)_3Si$ group are the bond angles about silicon. There are two normal bond angles of 108.4[4]° and a third larger angle of 117.0[10]°. Examination of the close contacts to the unique CH_3 group reveals that at or slightly below the van der Waal distance there is a close contact to the CH_3 group of the silicon linker, and another close contact to the *tert*-butyl group of the opposite ring. By far the shortest contact present, 3.68[3] Å, is to a carbon of the opposite cyclopentadienyl ring. All other distances and angles within the molecule are normal.

Figure 5. Exclusive synthesis of **rac-20**.

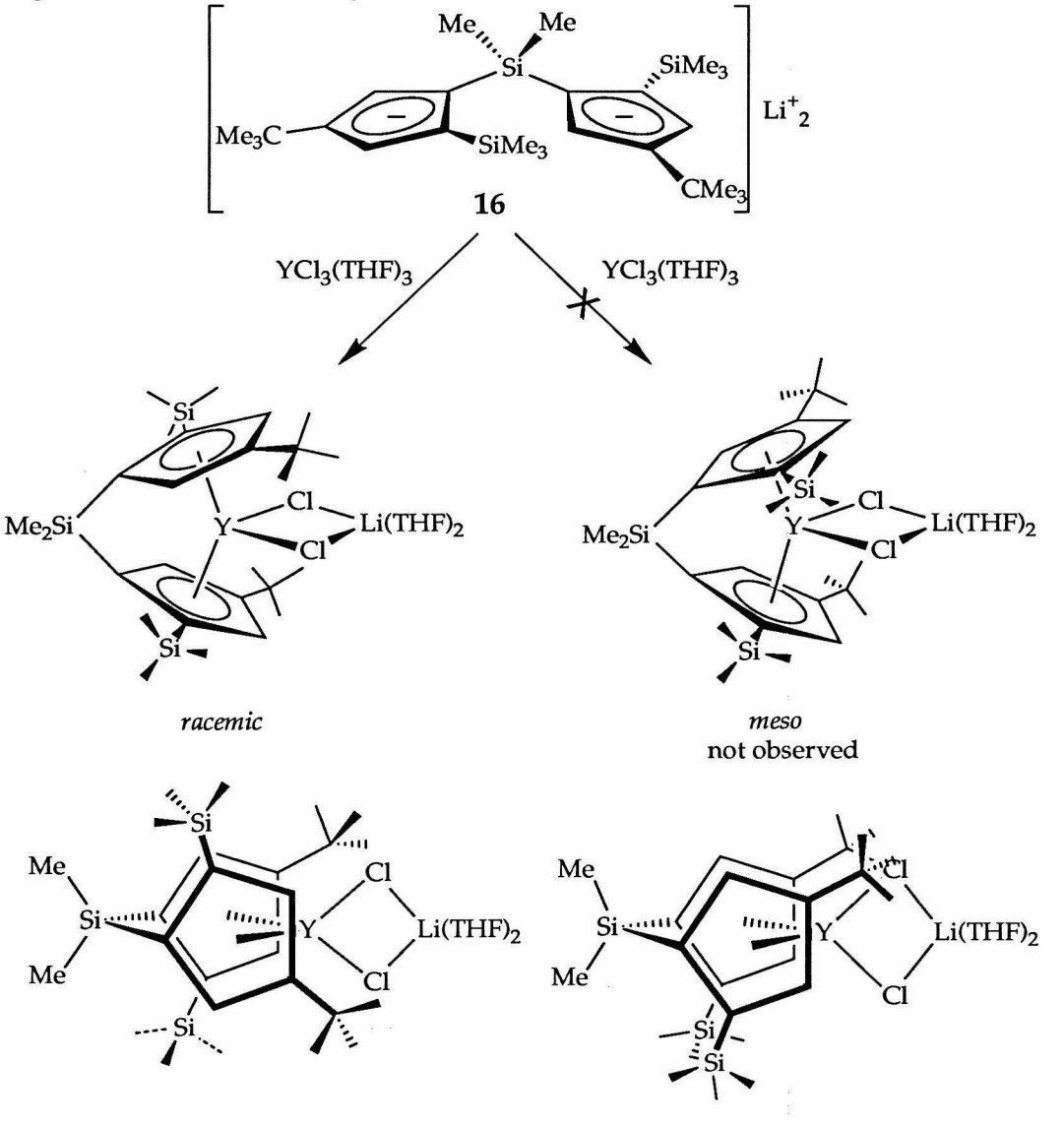
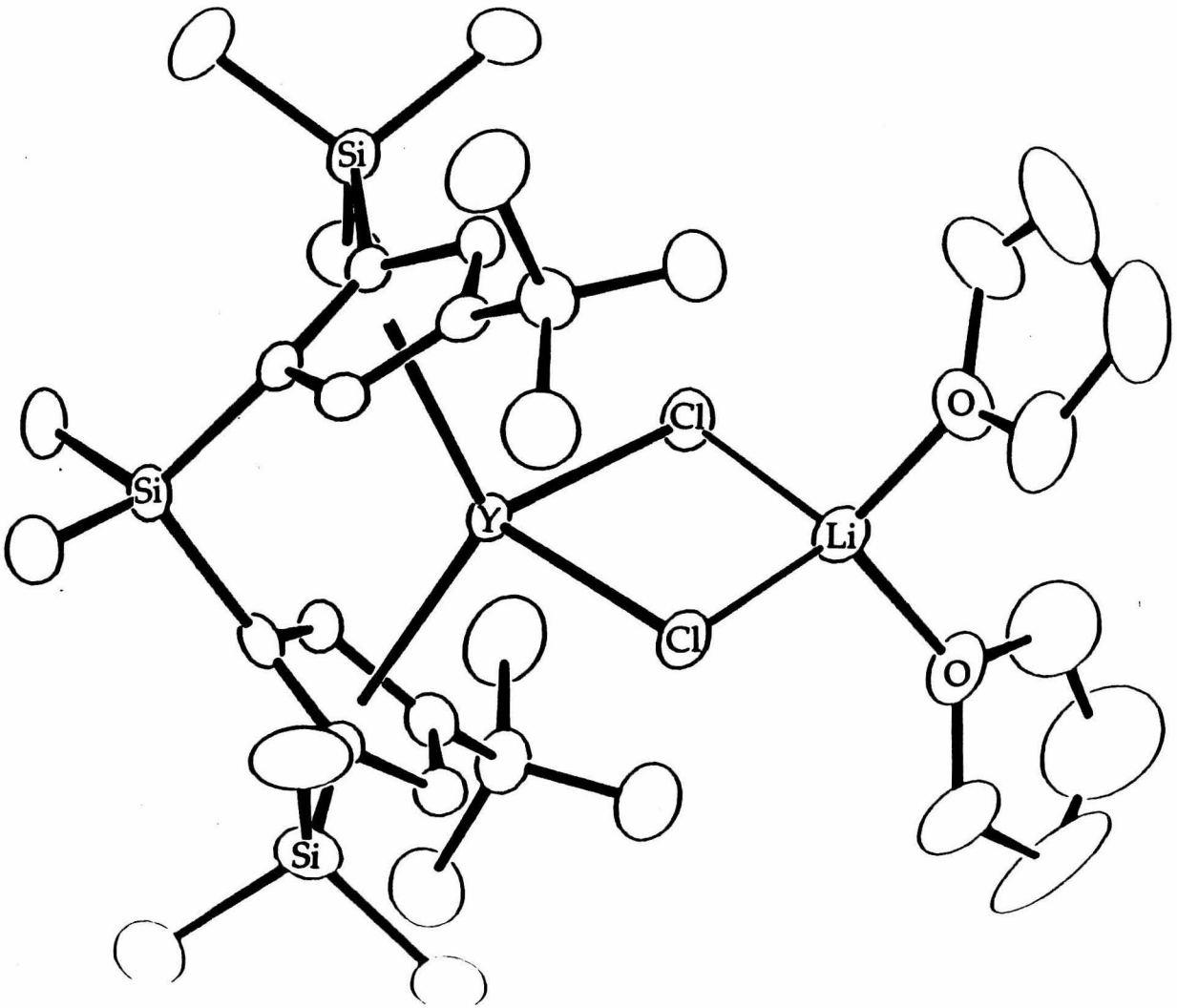
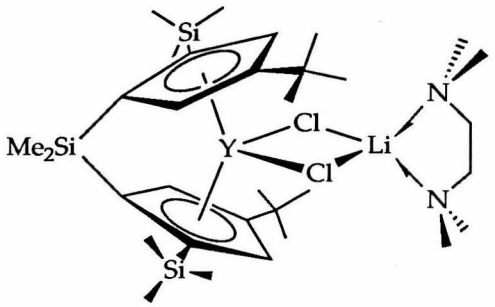


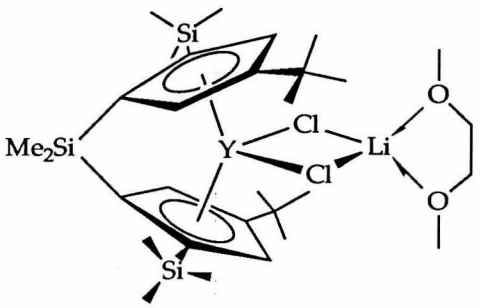
Figure 6. Molecular drawing of (*S*)-20 with all non-carbon atoms labelled, hydrogens have been omitted for clarity.



Attachment of either **17** or **18** to $YCl_3(THF)_3$ proceed in an analogous manner to the synthesis described above. The resulting products, **21** and **22** respectively, were found to be exclusively racemic and of a form very similar to that of **20**.



21

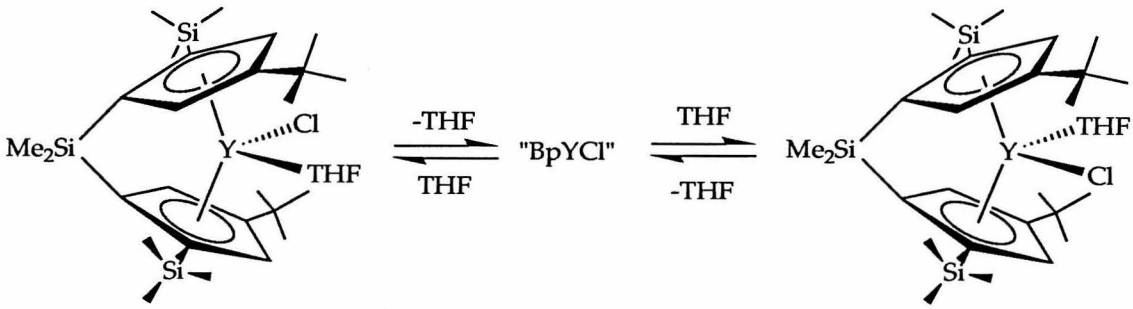


22

Transmetallation of $YCl_3(THF)_3$ with **19** occurs cleanly and in good yield upon refluxing overnight in either toluene or tetrahydrofuran. The identity of the final product is dependent upon the workup conditions employed. Removal of the volatiles in vacuo yields a white solid which can be slurried in toluene, filtered to remove KCl, followed by concentration of the filtrate and precipitation of the product with petroleum ether affording the base and halide free complex [BpYCl], **23**. Complex **23** is found to be exclusively the racemic isomer. Filtration of the crude reaction mixture in THF affords, after concentration and precipitation with petroleum ether, BpYCl(THF), **24**. The larger ionic radius of K^+ compared to Li^+ results in the former being too large to fit in the resultant Cl-Y-Cl cleft and thus KCl is readily displaced, allowing for the isolation of salt free **23** or **24**.[38]

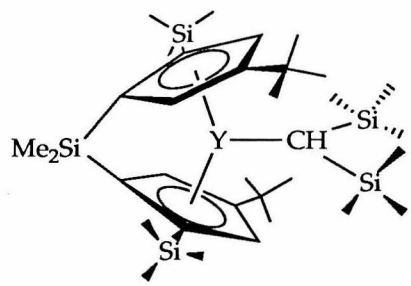
The ^1H NMR spectrum of **24** shows a species with overall C_2 symmetry which is indicative of a rapid THF dissociative/associative process that interconverts **24a** and **24b** such that the ligand resonances are rendered equivalent (vide infra). On the contrary, the corresponding pyridine adduct, **25**, does not undergo a similar rapid exchange process as evidenced by a doubling of each ^1H NMR resonance due to loss of C_2 symmetry. Conversion

of **24** to **23** is possible by simply dissolving **24** in toluene followed by removing the volatiles in vacuo.



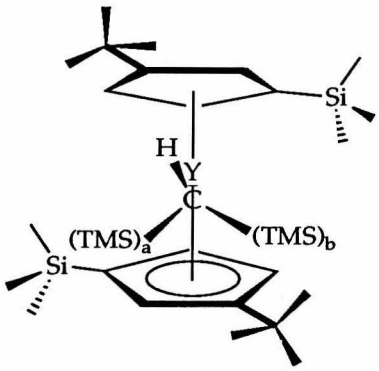
24a **24b**

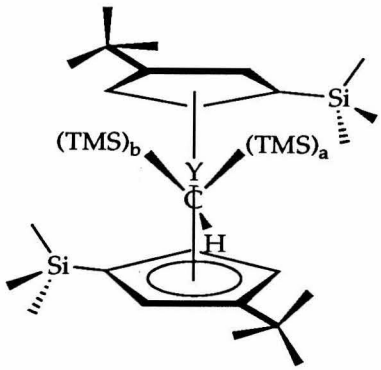
The synthesis of the alkyl derivative $BpYCH(Si(CH_3)_3)_2$, **26**, is conveniently accomplished by addition of $LiCH(Si(CH_3)_3)_2$ to either **20** or **23** in toluene followed by recrystallization from petroleum ether.



26

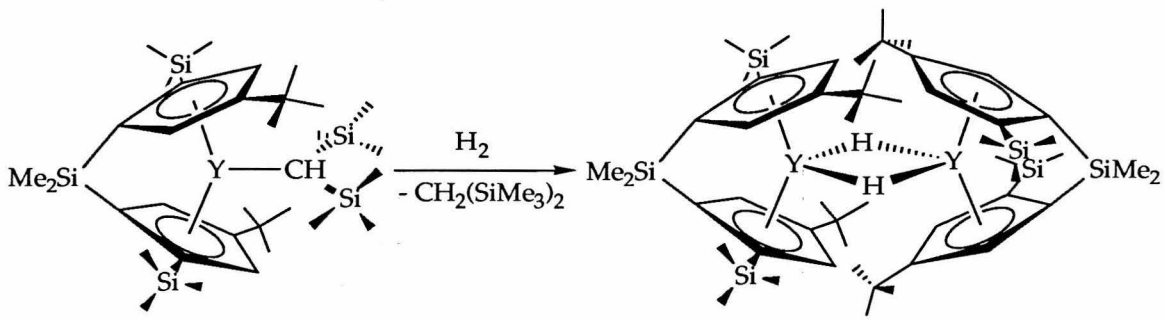
The hindered rotation of the $-CH(Si(CH_3)_3)_2$ group in **26** is evidenced by the loss of C_2 symmetry relating the two cyclopentadienyl rings.[39] A doubling of each ligand resonance is observed in the ^1H NMR spectrum. The two $Si(CH_3)_3$ groups of the $CH(Si(CH_3)_3)_2$ ligand are not equivalent irrespective of whether or not there is hindered rotation about the Y-C σ bond.





The alkylation of **21** and **22** with a variety of lithium alkyls, such as $LiCH(Si(CH_3)_3)_2$, $LiCH_2Si(CH_3)_3$, or $LiCH_2P(CH_3)_2$,[40] were unsuccessful. In each case the starting material was recovered essentially unchanged. Attempts to remove DME from **22** by heating under vacuum (150 °C, 1 μ Hg) only resulted in decomposition.

Hydrogenation of **26** proceeds cleanly and rapidly in petroleum ether to afford a dimeric hydride, **27**, and $H_2C(Si(CH_3)_3)_2$.



[rac-BpY-CH(SiMe$_3$)$_2$]

26

rac(S,S)-[BpY-H]$_2$

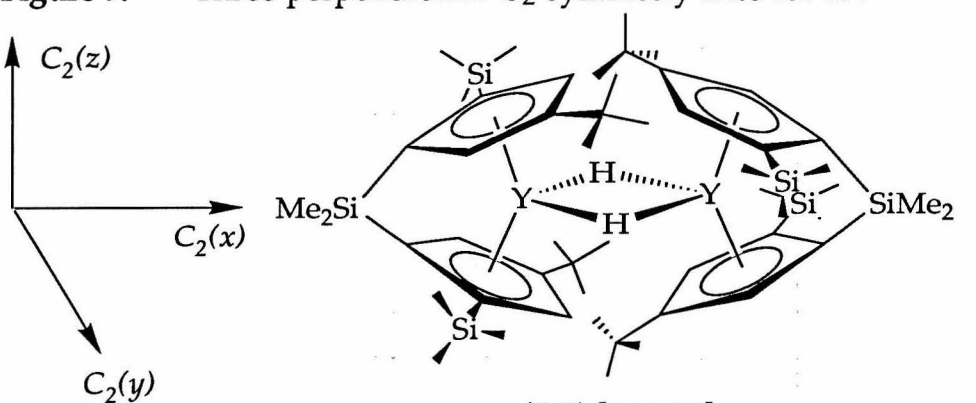
27

The formulation of **27** as a dimer is based upon the presence of a triplet at δ 4.87 ppm in the ^{1}H NMR spectrum assigned to the hydride resonances. The signal is a 1:2:1 triplet (J_{Y-H} = 31 Hz) due to coupling with two equivalent ^{89}Y nuclei (I=1/2; 100% natural abundance). The product is presumably the homochiral (*R,R*) and (*S,S*) dimers since the heterochiral (*R,S*) dimer is expected to have unfavorable steric interaction between the $C(CH_3)_3$ groups.

Slow cooling of a petroleum ether solution afforded single crystals that were of suitable quality for X-ray diffraction studies.

Complex **27** crystallizes in space group *P2/c* (#13) with a = 16.577 Å, b = 10.937 Å, c = 23.200 Å, and $\alpha = \gamma = 90^{o}$, $\beta = 127.55^{o}$. Complete refinement of the structure, however, proved impossible due to the presence of disordered solvent molecules within the unit cell. The metal-metal distance of 3.7 Å is within the range expected for a Y(μ-H)$_2$Y core based on crystallographic data for related lanthanide hydride dimers.[41] An interesting feature of **27** is that it has nearly perfect D_2 symmetry. The three perpendicular C_2 symmetry axes are easily seen with the aid of the coordinates shown in Figure 7. A molecular drawing of the (*S,S*) homochiral dimer is shown in Figure 8.

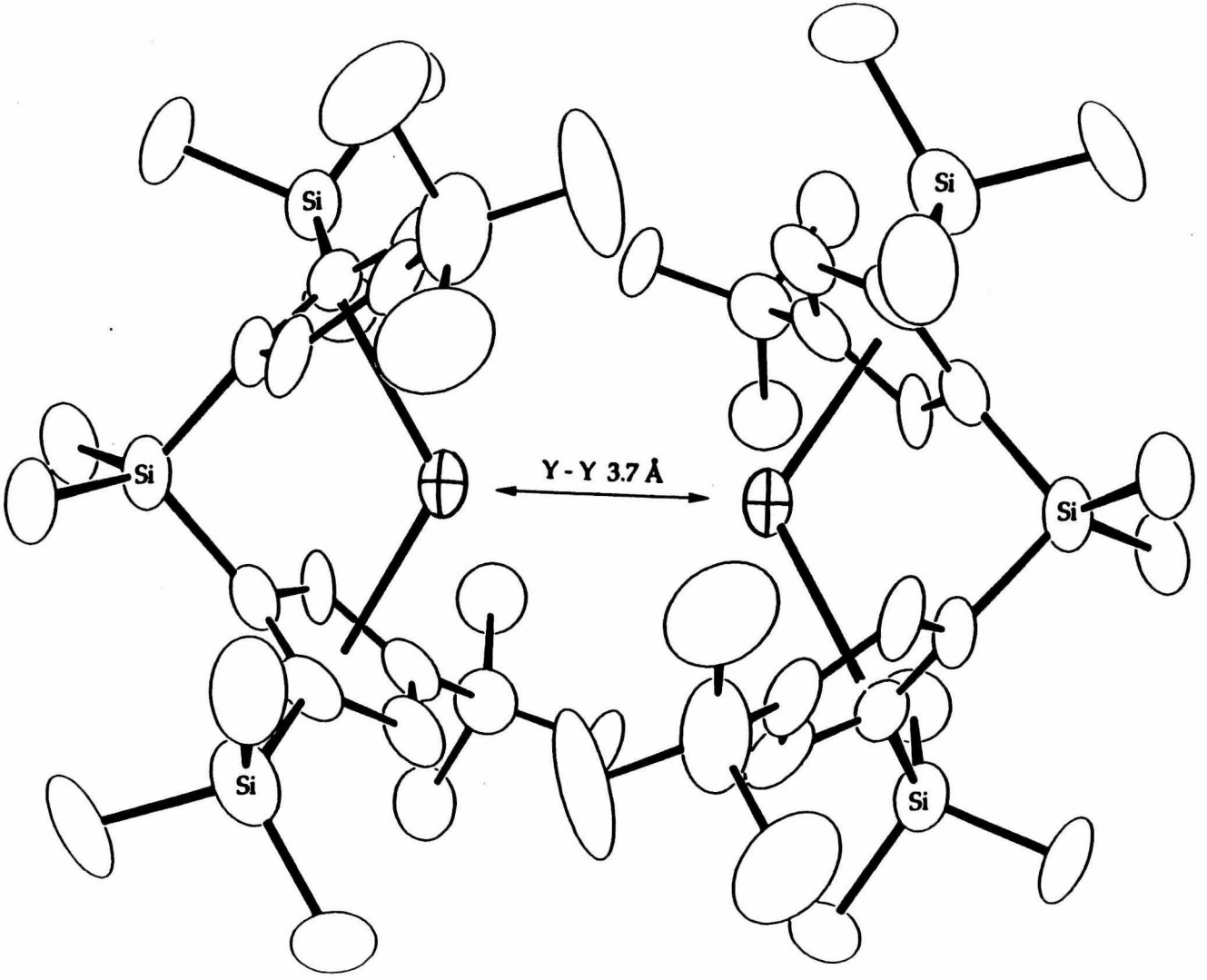
Figure 7. Three perpendicular C_2 symmetry axes for **27**.



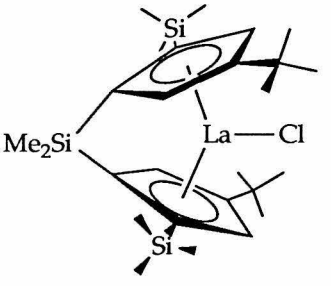
rac(S,S)-[BpY-H]$_2$

27

Figure 8. Molecular drawing of (*S*,*S*) **27** only non-carbon atoms labelled

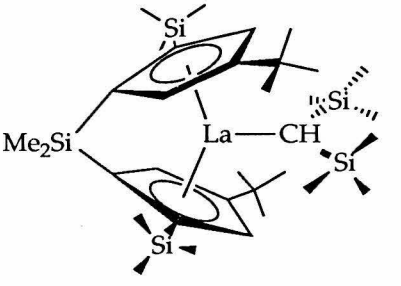


Due to the oligomeric nature of $LaCl_3$ the synthesis of BpLaCl, **28**, is most conveniently accomplished by first dissolving $LaCl_3$ in a combination of 6 M HCl and THF (1:1 v/v) followed by removal of the volatiles in vacuo and dehydration of a THF slurry using $SOCl_2$. The resultant $LaCl_3(THF)_x$ has sufficient solubility in refluxing THF for transmetallation with **19** to afford **28** in moderate yield. The product was found to be exclusively the racemic isomer. The low solubility of **28** in noncoordinating solvents precluded the determination of the solution molecular weight. Alkylation of **28** using $LiCH(Si(CH_3)_3)_2$ affords the alkyl derivative **29** in good yield. Hindered rotation about the La-C σ bond is evidenced by the doubling of all ligand resonances in the ^1H NMR spectrum of **29** in C_6D_6.



[rac-BpLa-Cl]

28



[rac-BpLa-CH(SiMe$_3$)$_2$]

29

Conclusions

The use of the sterically tailored ligand $[M^+]_2[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]^{2-}$ (M = Li, K) has allowed for the syntheses of several novel ansa-yttrocenes and ansa-lanthocenes. The most notable feature of this ligand is the two trimethylsilyl groups positioned proximal to the interannular bridge. The large steric demand of these two groups has lead to the exclusive synthesis of racemic ansa-metallocenes. The ease of preparation of this synthetically tailored ligand array should allow for the exploration into other transition metal systems. Given the importance of C_2 symmetric ansa-metallocenes in a variety of catalytic and stoichiometric transformations suggest that further investigations utilizing the Bp ligand are warranted.

Table V. ^{1}H NMR data for ligand salts **16-19.**

Compound	Assignment	δ (ppm)	J (Hz)
Li_2Bp **(16)**	C_5H_2	6.24, 6.08 (s)	
	$C(CH_3)_3$	1.22 (s)	
	$Si(CH_3)_2$	0.43 (s, br)	
	$Si(CH_3)_3$	-0.071 (s, br)	
$Li_2(TMEDA)_2Bp$ **(17)**	C_5H_2	6.53, 6.61 (d)	1.84
	$C(CH_3)_3$	1.55 (s)	
	$Si(CH_3)_2$	0.907 (s)	
	$Si(CH_3)_3$	0.294 (s)	
	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	1.83 (s)	
	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	1.48 (s)	
$Li_2(DME)_2Bp$ **(18)**	C_5H_2	6.71, 6.52 (s, br)	
	$C(CH_3)_3$	1.58 (s)	
	$Si(CH_3)_2$	0.89 (s)	
	$Si(CH_3)_3$	0.38 (s)	
	$(CH_3)OCH_2CH_2O(CH_3)$	2.92 (s)	
	$(CH_3)OCH_2CH_2O(CH_3)$	2.44 (s)	
K_2Bp **(19)**	C_5H_2	6.08, 6.36 (d)	1.8
	$C(CH_3)_3$	1.28 (s)	
	$Si(CH_3)_2$	1.09 (s)	
	$Si(CH_3)_3$	0.54 (s)	

Table VI. ^{1}H NMR data for LiCl complexes **20-22.**

Compound	Assignment	δ (ppm)	J (Hz)
BpY(μ-Cl)$_2$Li(THF)$_2$ **(20)**	C_5H_2	7.00, 6.67 (s)	
	$C(CH_3)_3$	1.51 (s)	
	$Si(CH_3)_2$	1.07 (s)	
	$Si(CH_3)_3$	0.60 (s)	
	THF α-CH_2	3.40 (s, br)	
	THF β-CH_2	1.25 (s, br)	
BpY(μ-Cl)$_2$Li(TMEDA) **(21)**	C_5H_2	6.63, 6.92 (d)	2.0
	$C(CH_3)_3$	1.48 (s)	
	$Si(CH_3)_2$	1.02 (s)	
	$Si(CH_3)_3$	0.55 (s)	
	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	1.94 (s)	
	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	1.27 (s)	
BpY(μ-Cl)$_2$Li(DME) **(22)**	C_5H_2	7.00, 6.64 (d)	2.05
	$C(CH_3)_3$	1.51 (s)	
	$Si(CH_3)_2$	1.04 (s)	
	$Si(CH_3)_3$	0.58 (s)	
	$(CH_3)OCH_2CH_2O(CH_3)$	2.97 (s)	
	$(CH_3)OCH_2CH_2O(CH_3)$	2.50 (s)	

Table VII. ^{1}H NMR data for complexes **23-25.**

Compound	Assignment	δ (ppm)	J (Hz)
BpYCl (**23**)	C_5H_2	6.93, 6.60 (d)	2.00
	$C(CH_3)_3$	1.50 (s)	
	$Si(CH_3)_2$	1.06 (s)	
	$Si(CH_3)_3$	0.62 (s)	
BpYCl(THF) (**24**)	C_5H_2	6.92, 6.58 (d)	2.12
	$C(CH_3)_3$	1.49 (s)	
	$Si(CH_3)_2$	1.05 (s)	
	$Si(CH_3)_3$	0.61 (s)	
	THF α-CH_2	3.46 (t, br)	
	THF β-CH_2	1.40 (t, br)	
BpYCl(Pyr) (**25**)	C_5H_2	7.16, 6.60, 6.53, 5.35 (d)	2.2 Hz
	$C(CH_3)_3$	1.44, 1.06 (s)	
	$Si(CH_3)_2$	1.03, 0.85 (s)	
	$Si(CH_3)_3$	0.42, 0.66 (s)	
	C_6H_5N	8.79, 6.69, 6.37(m)	

Table VIII. ^{1}H NMR data for complexes **26** and **27.**

Compound	Assignment	d (ppm)	J (Hz)
BpYCH(TMS)$_2$ (**26**)	C_5H_2	7.31, 6.70, 6.48, 6.36 (d)	2.0, 2.1
	$C(CH_3)_3$	1.34, 1.20 (s)	
	$Si(CH_3)_2$	0.92	
	$Si(CH_3)_3$	0.41, 0.34, 0.28, 0.18 (s)	
	YC*H*	0.05 (d)	0.36 $^2J_{(Y-H)}$
[BpY-H]$_2$ (**27**)	C_5H_2	6.93, 6.43 (s)	
	$C(CH_3)_3$	1.35 (s)	
	$Si(CH_3)_2$	1.01 (s)	
	$Si(CH_3)_3$	0.38 (s)	
	YH	4.87 (t)	31 $J_{(Y-H)}$

Table IX. ^{1}H NMR data for complexes **28** and **29.**

Compound	Assignment	δ (ppm)	J (Hz)
BpLaCl (**28**)	C_5H_2	6.57, 6.31 (s)	
	$C(CH_3)_3$	1.23 (s)	
	$Si(CH_3)_2$	0.83 (s)	
	$Si(CH_3)_3$	0.31 (s)	
BpLaCH(TMS)$_2$ (**29**)	C_5H_2	7.09, 6.82, 6.57, 6.45 (d)	2.1
	$C(CH_3)_3$	1.33, 1.27 (s)	
	$Si(CH_3)_2$	0.905, 0.900 (s)	
	$Si(CH_3)_3$	0.40, 0.33, 0.30, 0.22 (s)	
	LaCH	-0.343 (s)	

Table X. $^{13}C[^{1}H]$ NMR data for complexes **23-25.**

Compound	Assignment	δ (ppm)
BpYCl (**23**)	C_5H_2	118.3, 120.0, 124.9, 146.7
	$C(CH_3)_3$	33.03
	C(CH3)3	31.92
	$Si(CH_3)_2$	0.527
	$Si(CH_3)_3$	2.78
BpYCl(THF) (**24**)	C_5H_2	148.1, 146.7, 124.9, 120.0, 118.3
	$C(CH_3)_3$	33.03
	$C(CH_3)_3$	31.90
	$Si(CH_3)_2$	0.546
	$Si(CH_3)_3$	2.806
	THF α-CH_2	67.84
	THF β-CH_2	25.65
BpYCl(Pyr) (**25**)	C_5H_2	209.4, 148.1, 147.8, 126.3, 124.3, 123.3, 122.7, 121.6, 118.7, 116.2
	$C(CH_3)_3$	32.25, 32.98
	$C(CH_3)_3$	31,44, 31.70
	$Si(CH_3)_2$	0.04, 1,26
	$Si(CH_3)_3$	2.49, 3.28
	C_6H_5N	151.1, 139.4, 128.9, 127.1, 124.7

Table XI. $^{13}C[^1H]$ NMR data for complexes **26** and **27.**

Compound	Assignment	δ (ppm)
$BpYCH(TMS)_2$ (**26**)	C_5H_2	150.7, 150.1, 126.8, 126.2, 125.8, 125.1, 125.0, 124.9, 120.4, 122.2
	$C(CH_3)_3$	33.3, 33.0
	$C(CH_3)_3$	32.3, 32.0
	$Si(CH_3)_2$	2.37, 2.70, 3.32, 5.93
	$Si(CH_3)_3$	0.141, 0.443
	Y-C	26.0 (d $^1J(^{89}Y\text{-}^{13}C)$ = 34.2 Hz)
$[BpY\text{-}H]_2$ (**27**)	C_5H_2	153.9, 145.1, 141.3, 122.0, 120.5
	$C(CH_3)_3$	31.1
	$C(CH_3)_3$	33.9
	$Si(CH_3)_2$	3.63
	$Si(CH_3)_3$	2.94

Table XII. $^{13}C[^1H]$ NMR data for complexes **28** and **29.**

Compound	Assignment	δ (ppm)
BpLaCl (**28**)[a]	C_5H_2	123.68, 126.00, 127.42, 128.84, 129.63
	$C(CH_3)_3$	32.92
	$C(CH_3)_3$	32.33
	$Si(CH_3)_2$	1.064
	$Si(CH_3)_3$	2.604
$BpLaCH(TMS)_2$ (**29**)	C_5H_2	124.43, 124.78, 126.22, 126.36, 126.99, 127.84, 130.86, 132.34, 151.36, 152.18
	$C(CH_3)_3$	32.63, 38.72
	$C(CH_3)_3$	32.40, 32.82
	$Si(CH_3)_2$	1.402, 2.052
	$Si(CH_3)_3$	0.784, 2.380, 4.026, 5.319

a) Spectrum taken in THF-d_8.

Experimental Section

General Considerations. All manipulations requiring air and moisture sensitive work were performed using Schlenk, high vacuum and inert atmosphere techniques as described previously.[42] Solvents were predried by distillation from appropriate drying agents, stored in solvent pots over either Na/benzophenone or titanocene,[43] and were vacuum-distilled from the solvent pots into reaction vessels immediately prior to use. All other reagents were purified using standard methods.[44] Elemental analyses were performed by Fenton Harvey of the California Institute of Technology Elemental Analysis Facility. When indicated V_2O_5 was added directly to the sample as a co-oxidant to assist in combustion. ^1H and $^{13}C[^1H]$ NMR spectra for all new complexes are shown in Tables V-XII.

Instrumentation. NMR spectra were recorded on a General Electric QE-300 Spectrometer (^1H, 300.1 MHz; ^{13}C, 75 MHz). All spectra were recorded in C_6D_6 unless otherwise noted. Spectra are referenced versus the residual protio signal at δ 7.15 ppm (^1H) and versus the center resonance of the benzene-d_6 ^{13}C triplet at δ 128.0 ppm (^{13}C).

Reagents. Dicyclopentadiene was thermally cracked and the distilled cyclopentadiene was stored at -60 °C. Methyl lithium was obtained as a 1.4 M solution in diethyl ether (Aldrich) and n-Butyl lithium as a 1.6 M solution in hexanes (Aldrich); both were used without further purification. Dichlorodimethylsilane and chlorotrimethylsilane were distilled from CaH_2 immediately prior to use. $YCl_3(THF)_3$ was prepared using a procedure identical to that reported by Manzer for the corresponding scandium complex.[45] KO*t*-Bu was sublimed prior to use and stored in an inert atmosphere drybox. $Li[(CH_3)_3C\text{-}C_5H_4]$ was prepared in nearly quantitative yield by the addition of methyl lithium to 6,6 dimethylfulvene in a procedure analogous to that reported by Sullivan and Little.[46] $Li_2[(3\text{-}(CH_3)_3C\text{-}C_5H_3)_2SiMe_2]$ (Li_2Dp) was prepared as reported previously.[47] $LiCH(Si(CH_3)_3)_2$ was prepared by lithium-halogen exchange of $ClCH(Si(CH_3)_3)_2$ (Aldrich) by the method of Cowley.[48]

6,6-Dimethylfulvene. A modification of a literature procedure[49] is given that is amenable to multigram (~100 g) preparations. Cyclopentadiene (27 g, 0.41 mol) and acetone (60 mL, 0.82 mol) were combined with 250 ml methanol in a 500 mL round bottom flask. Pyrrolidine (3.3 mL, 0.04 mol, 10 mol%) was added and the solution immediately became yellow. After 14 h of stirring at room temperature the reaction was halted by addition of 250 ml of Et_2O and 250 mL of 5% acetic acid. The layers were separated and the aqueous layer washed twice with 100 mL portions of Et_2O. The ether layers were combined and washed twice with 100 mL portions of saturated aqueous $NaHCO_3$. The ether solution was dried over $MgSO_4$. Removal of the Et_2O by rotorary evaporator followed by vacuum distillation gave 39.3 g (90%) of an orange liquid that was identical by ^1H NMR spectroscopy to that previously reported.

$(CH_3)_2Si((CH_3)_3CC_5H_3Si(CH_3)_3)_2$ (BpH_2), 15. A 250 mL round bottom flask was charged with Li_2Dp (16.13 g, 51.6 mmol) and THF (125 mL) was added by vacuum transfer. Chlorotrimethylsilane (32 mL, 250 mmol) was added by vacuum transfer and the reaction allowed to stir at room temperature for 24 h. The volatiles were removed in vacuo. Petroleum ether was added and the LiCl removed by filtration. Removal of the volatiles in vacuo and vacuum distillation of the residual liquid (150 °C, 1μ Hg) yielded 16.75 g (73%) of a thick viscous yellow oil. Due to the large number of potential regioisomers resulting from silyl migration about the cyclopentadiene rings (vide supra) NMR spectroscopic characterization of the product proved difficult. Satisfactory elemental analysis was obtained. Upon standing for several weeks, the yellow liquid solidified to a low melting solid.

$Li_2[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]$ (Li_2Bp), 16. To a solution of Li_2Dp (6.01 g, 19.24 mmol) in THF was added $ClSi(CH_3)_3$ (15.5 ml, 122.1 mmol, 6.3 equiv.). The resulting solution was stirred at ambient temperature for 20 h. The volatiles were removed in vacuo. The resulting yellow oil was dissolved in petroleum ether and the LiCl removed by filtration. The filtrate was cooled to 0 °C and n-BuLi (26 ml of a 1.6 M solution, 41.6 mmol, 2.17 equiv.) was added by syringe against an argon counterflow. After several days a white crystalline product was isolated by filtration. Overall yield for 2 crops of crystals was 2.06 g, (23.7%). Elemental analysis calculated for $C_{26}H_{46}Li_2Si_3$: C, 68.37; H, 10.15. Found C, 64.87, 65.69; H, 10.39, 10.55.

$Li_2[(CH_3)_2NCH_2CH_2N(CH_3)_2]_2[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]$ ($Li_2(TMEDA)_2Bp$), 17. To a petroleum ether solution of **15** (0.886 g, 1.99 mmol) was added TMEDA (0.48 g, 4.31 mmol). A 1.6 M solution of n-BuLi (2.5 mL, 4.0 mmol) was added in a single portion. After stirring for several hours at ambient temperature **16** had precipitated from solution and was isolated by filtration. Yield 0.866 g (63%). Elemental analysis calculated for $C_{38}H_{78}Li_2N_4Si_3$: C, 66.22; H, 11.41; N, 8.13. Found C, 70.84, 68.58, 66.78; H, 11.94, 11.66, 11.42; N, 8.78, 8.35, 7.86; added V_2O_5 used to aid combustion.

$Li_2(CH_3OCH_2CH_2OCH_3)_2[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]$ ($Li_2(DME)_2Bp$), 18. To a petroleum ether solution of **15** (0.860 g, 1.88 mmol) was added DME (0.706 g, 7.88 mmol). A 1.6 M solution of n-BuLi (2.4 mL, 3.84 mmol) was added in a single portion. After stirring for 12 h at ambient temperature the reaction mixture was cooled to -30 °C overnight. The resulting white precipitate was isolated by filtration and dried in vacuo, yield 0.433 g (34.2%). Elemental analysis calculated for $C_{34}H_{66}Li_2O_4Si_3$: C, 64.11; H, 10.44. Found C, 64.13, 64.61, 63.90, 65.07; H, 10.23, 10.61, 10.55. 10.76; added V_2O_5 used to aid combustion.

$K_2[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]$ (K_2Bp), 19. 15 (13.90 g, 30.4 mmol) was dissolved in THF (300 mL). KO*t*Bu (6.82 g, 60.8 mmol) was added and the reaction stirred at room temperature for 22 h. The volatiles were removed in vacuo. The resulting solid was powdered and the solid was heated to 60 °C

under dynamic vacuum overnight to remove the last traces of *tert*-BuOH. Yield 14.67 g (90%). Elemental analysis calculated for $C_{26}H_{46}K_2Si_3$: C, 59.93; H, 8.90. Found C, 59.45, 60.80; H, 8.93, 8.92; added V_2O_5 used to aid combustion.

$[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]Y(\mu\text{-}Cl)_2Li(C_4H_8O)_2$ ($BpY(\mu\text{-}Cl)_2Li(THF)_2$, 20. $YCl_3(THF)_3$ (0.458 g, 1.13 mmol) and **16** (0.0506 g, 1.11 mmol) were dissolved in 30 mL of toluene. The solution was warmed to 78 °C for 12 h. The reaction mixture was cooled to room temperature the LiCl removed by filtration and washed once with 5 mL toluene. The volatiles were removed in vacuo. Petroleum ether was added and the resulting white precipitate isolated by filtration. Yield 0.309 g, (39%). Elemental analysis calculated for $C_{34}H_{62}Cl_2LiOSi_3Y$: C, 54.17; H, 8.29%. Found C, 54.30; H, 8.15; added V_2O_5 used to aid combustion.

$[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]Y(\mu\text{-}Cl)_2Li((CH_3)_2NCH_2CH_2N(CH_3)_2)$ ($BpY(\mu\text{-}Cl)_2Li(TMEDA)$, 21. $YCl_3(THF)_3$ (0.597 g, 1.45 mmol) and **17** (1.02 g, 1.48 mmol) were dissolved in 35 mL of toluene. The resulting slurry was heated to 75 °C overnight. The solution was filtered to remove LiCl and the volatiles removed in vacuo. Petroleum ether was added and the white solid isolated by filtration, yield 0.946 g (88%). Elemental analysis calculated for $C_{32}H_{62}Cl_2LiSi_3N_2Y$: C, 52.95; H, 8.61; N, 3.86. Found C, 52.85, 54.28, 53.30; H, 8.57, 8.85, 8.82; N, 3.46, 3.37, 3.26; added V_2O_5 used to aid combustion.

$[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]Y(\mu\text{-}Cl)_2Li(CH_3OCH_2CH_2OCH_3)$ ($BpY(\mu\text{-}Cl)_2Li(DME)$, 22. A 100 mL round bottom flask was charged with **17** (0.452 g, 0.696 mmol) and $YCl_3(THF)_3$ (0.291 g, 0.707 mmol). Toluene (50 mL) was added and the reaction warmed to 80 °C for 60 h. The LiCl was removed by filtration, concentration of the filtrate followed by precipitation with petroleum ether afforded 0.303 g (62%) of **22** as a white solid. Elemental analysis calculated for $C_{30}H_{56}Cl_2LiO_2Si_3Y$: C, 51.45; H, 8.14. Found C, 51.11, 50.71; H, 7.88, 7.84; added V_2O_5 used to aid combustion.

[[$(CH_3)_2$Si(4-$(CH_3)_3$C-2-$(CH_3)_3$Si-$C_5H_2)_2$]Y(μ-Cl)]$_2$ (BpY(μ-Cl)$_2$, 23. A 250 mL round bottom flask was charged with **18** (4.0 g, 7.5 mmol), $YCl_3(THF)_3$ (3.09 g, 7.5 mmol), THF (100 mL) and the reaction mixture refluxed for 40 h. The volatiles were removed in vacuo, and toluene added and removed in vacuo to render the solid free of THF. Toluene was again added and the KCl removed by filtration. Concentration of the filtrate followed by precipitation with petroleum ether gave 3.17 g (75%) of **23** as a white solid. Elemental analysis calculated for $C_{26}H_{46}Si_3Y$: C, 58.72; H, 8.72. Found C, 49.86, 49.95; H, 7.58, 7.71; added V_2O_5 used to aid combustion.

[$(CH_3)_2$Si(4-$(CH_3)_3$C-2-$(CH_3)_3$Si-$C_5H_2)_2$]YCl(C_4H_8O) (BpYCl·THF), 24. A 250 ml round bottom flask was charged with **19** (5.01 g, 9.4 mmol), $YCl_3(THF)_3$ (3.86 g, 9.4 mmol) and equipped with a reflux condenser. Tetrahydrofuran (175 mL) was added and the reaction refluxed for 40 h. The volatiles were removed in vacuo. Toluene was added and the KCl removed by filtration. Concentration of the filtrate followed by precipitation of the product by addition of petroleum ether gave 2.82 g (53%) of **24** as a white solid. Elemental analysis calculated for $C_{30}H_{54}ClOSi_3Y$: C, 56.63; H, 8.20. Found C, 51.34, 50.09, 50.81, 50.33, 50.91; H, 7.69, 7.81, 7.71, 7.56, 7.67; added V_2O_5 used to aid combustion.

[$(CH_3)_2$Si(4-$(CH_3)_3$C-2-$(CH_3)_3$Si-$C_5H_2)_2$]YCl(C_5H_5N) (BpYCl·Pyridine), 25. A 50 ml round bottom flask was charged with **24** (0.200 g, 0.313 mmol) and 25 mL of toluene. Pyridine (0.14 ml, 1.73 mmol) was added by vacuum transfer. The solution was stirred at ambient temperature for 24 h. The volatiles were removed in vacuo leaving **25** as a white solid. Yield 0.148 gm (76%). Elemental analysis calculated for $C_{29}H_{51}ClNSi_3Y$: C, 55.97; H, 8.26; N 2.25. Found C, 52.50, 54.19, 54.09, 56.37; H, 7.50, 7.64, 7.46, 7.86; N, 1.90, 1.78, 1.80, 2,28; added V_2O_5 used to aid combustion.

[$(CH_3)_2$Si(4-$(CH_3)_3$C-2-$(CH_3)_3$Si-$C_5H_2)_2$]YCH($Si(CH_3)_3)_2$ (BpYCH(TMS)$_2$), 26. **(A) 20** (0.552 g, 0.776 mmol) and $LiCH(Si(CH_3)_3)_2$ (0.135 g, 0.812 mmol) were dissolved in 50 mL of toluene. The solution was stirred at ambient temperature for 12 h. The volatiles were removed in vacuo and the resulting solid extracted into petroleum ether. The LiCl was removed by filtration. Removal of the volatiles gave **26** as an off white solid, yield 0.419 g (78%). Elemental analysis calculated for $C_{33}H_{65}Si_5Y$: C, 57.34; H, 9.48. Found C, 56.97, 56.66; H, 9.38, 9.25; added V_2O_5 used to aid combustion. **(B) 23** (1.25 g, 2.20 mmol) and $LiCH(Si(CH_3)_3)_2$ (0.454 g, 2.73 mmol) were combined in a 50 mL round bottom flask. Toluene (40 mL) was added and the reaction stirred for 24 h. The volatiles were removed in vacuo and the product extracted with petroleum ether. The LiCl was removed by filtration. Concentration of the filtrate and cooling to -78 °C gave **26** as a white solid after isolation by filtration, Yield 1.00 g, (65.8%). Elemental analysis calculated for $C_{33}H_{65}Si_5Y$, C 57.34; H 9.48. Found C, 55.98, 56.52; H, 9..24, 9.97; added V_2O_5 used to aid combustion.

[[$(CH_3)_2$Si(4-$(CH_3)_3$C-2-$(CH_3)_3$Si-$C_5H_2)_2$]Y-H]$_2$ (BpYH)$_2$, 27. **26** (0.271 g, 0.392 mmol) was dissolved in 25 mL of petroleum ether. Hydrogen (1 atm) was admitted and the reaction stirred for 7 h. The solution was concentrated and cooled to -78 °C. **27** was isolated as a pale yellow microcrystalline solid by filtration. Yield 0.093 g, 45%. Elemental analysis calculated for $C_{26}H_{47}Si_3Y$: C, 58.61; H, 8.89. Found C, 58.78, 59.20, 58.98; H, 9.15, 9.08, 9.26; added V_2O_5 used to aid combustion.

[$(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2$]LaCl (BpLaCl), 28. Anhydrous $LaCl_3$ (1.95 g, 7.95 mmol, AESAR 20 mesh) was ground to a fine powder. The white powder was slurried with THF (4 mL) and HCl (4 mL, 6 M) and heated to 80 °C in a sealed bomb. After 3 h two clear immiscible layers had formed. The volatiles were removed in vacuo and fresh THF added. The resulting slurry was dehydrated with $SOCl_2$ (10 mL). The volatiles were once again removed in vacuo to yield $LaCl_3(THF)_x$ as an off-white solid that was not characterized further but used directly in the next step. **19** (4.06 g, 7.61 mmol) and the $LaCl_3(THF)_x$ were combined in a 250 mL round bottom flask equipped with a reflux condenser. THF (100 mL) was added and the reaction refluxed for 40 h. The product was slurried in toluene and isolated by filtration. Yield 2.06 g, 43%. Elemental analysis calculated for $C_{26}H_{46}ClLaSi_3$: C, 50.59; H, 7.51. Found C, 54.98, 53.52; H, 8.08, 7.96; added V_2O_5 used to aid combustion.

[$(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2$]LaCH$(Si(CH_3)_3)_2$ (BpLaCH(TMS)$_2$), 29. A 100 ml round bottom flask was charged with **28** (0.700 g, 1.11 mmol) and $LiCH(Si(CH_3)_3)_2$ (0.190 g, 1.14 mmol). Toluene (60 ml) was added and the reaction stirred at ambient temperature for 24 h. The volatiles were removed in vacuo and the product extracted with petroleum ether. LiCl was removed by filtration. Removal of the volatiles from the filtrate afforded 0.470 g, 57%, of **29** as a white solid. Elemental analysis calculated for $C_{33}H_{56}LaSi_5$: C, 53.47; H, 8.84. Found C, 53.05, 55.30, 52.07, 53.49, 52.36; H, 8.92, 9.04, 8.97, 9.17, 9.01; added V_2O_5 used to aid combustion.

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Chapter 3

Iso-Specific α–Olefin Polymerization with a Single Component Catalyst

Abstract: The alkyl species **26** is an excellent intiator for ethylene polymerization. The dimeric hydride **27** catalyzes the polymerization of propylene (25% v/v in methylcyclohexane) and neat samples of 1-butene, 1-pentene, and 1-hexene to moderately high molecular weight polymers. ^{13}C NMR of the resulting polymers at the pentad analysis level show a remarkably high degree of isotacticity for all samples. The presumed origins of this isospecificity are presented.

Introduction

Homogeneous Ziegler-Natta polymerization was pioneered by the independent discoveries of Natta and Breslow that combinations of titanocene dichloride and either triethylaluminum or diethylaluminum chloride produce a catalyst capable of polymerizing ethylene.[1] However, these systems were found to have no activity towards the polymerization of propylene. It was later observed[2] that the addition of small amounts of water to various group IV metallocene alkylaluminum catalyst mixtures resulted in increased polymerization activity. This discovery eventually lead to the development of a halide free aluminum co-catalyst.[3] The addition of water to solutions of trimethyl aluminum in the ratio of between 1:2 to 1:5 is found to give alumoxanes that exhibit maximum polymerization activity; the resultant structures are known to consist of several cyclic and linear fragments comprised of -O-Al(CH_3)- building blocks.[4] The use of methyl alumoxane (MAO), generally in large excess, in conjunction with group 4 metallocenes is found to produce catalysts capable of polymerizing ethylene, propylene, and higher α-olefins.

An original proposal[5] that the active center in these polymerization catalysts is a cationic metallocene alkyl species has been verified by the extensive work of Jordan and co-workers.[6] Several discrete zirconocene alkyl cations have been isolated and fully characterized, generally as stable THF or acetonitrile adducts. Investigations have shown that these zirconocene alkyl cation adducts do indeed undergo several key steps in Ziegler-Natta catalysis. Ethylene can be rapidly polymerized by these Lewis base stabilized cations to polyethylene. However, these stabilized cationic systems are found to only oligomerize propylene and higher α-olefins.

The large excess of MAO required for activation of zirconocene dichloride severely hampers any attempt at in situ investigation of the active species, as well as greatly increasing the cost of performing polymerizations. Recently tremendous effort has been directed toward the use of stoichiometric or near stoichiometric activators in conjunction with preformed zirconocene dialkyls. The use of non-coordinating solvents during generation of the

cations should result in base free 14 electron zirconocene alkyls that promise to exhibit α-olefin polymerization activity. The relative simplicity of these catalyst systems should make them more amenable to mechanistic study.

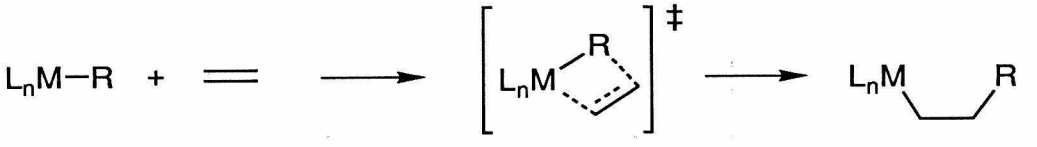
Perhaps the most successful strategy for generation of a base-free alkyl cation has been the work of Turner and Hlatky.[7] A key discovery was the use of the robust non-nucleophilic anion $[B(C_6F_5)_4]^-$ for the stabilization of the reactive $[Cp_2Zr(CH_3)]^+$ fragment. Generation of the alkyl cation is readily accomplished by protonation of $Cp_2Zr(CH_3)_2$ with the dimethylanilinium salt $[(C_6H_5)N(CH_3)_2H]^+[B(C_6F_5)_4]^-$ in non-coordinating solvents . Alternatively methyl anion abstraction from $Cp_2Zr(CH_3)_2$ can be performed using the stable carbocation $[(C_6H_5)_3C]^+$, once again use of non-coordinating solvents and the $[B(C_6F_5)_4]^-$ counterion results in very active α-olefin polymerization catalysts.[8] A clever method for generation of a zirconocene alkyl cation utilizes the high Lewis acidity of $B(C_6F_5)_3$ to abstract a methyl anion from $Cp_2Zr(CH_3)_2$ forming $[Cp_2Zr(CH_3)]^+[CH_3B(C_6F_5)_3]^-$. This abstraction is reversible as evidenced by dynamic NMR studies, however, polymerization activity is observed.[9]

Parallel investigations by several different groups on the isoelectronic neutral group III and (ignoring *f* electrons) lanthanide metallocene analogs has further revealed several key mechanistic aspects of Ziegler-Natta catalysis. In a series of elegant experiments, Watson demonstrated that the bispentamethylcyclopentadienyllutetium fragment ($(\eta^5\text{-}C_5(CH_3)_5)_2LuR$) is capable of undergoing olefin insertion reactions that serve as models for polymer chain propagation. She also observed β-hydride and β-alkyl eliminations as possible chain termination pathways.[10] This system only oligomerizes propylene as the measured rate of elimination is comparable to the bimolecular rate of olefin insertion. With ethylene, the rate of polymerization is much greater than that of chain termination, and consequently polymerization is observed. Related work has shown that complexes of the type $(\eta^5\text{-}C_5(CH_3)_5)_2M\text{-}R$ (M = Y, Nd, Sm, Lu) are generally very good ethylene polymerization catalysts.[11] However, these metallocenes are found to only oligomerize propylene.

Previous work in the Bercaw group with a family of scandocene alkyls has also demonstrated several key steps in the postulated mechanism of Ziegler-Natta catalysis. Permethylscandocenemethyl was found to oligomerize ethylene in a living fashion at low temperature.[12] Propylene was found to undergo vinylic C-H bond activation presumably due to overriding steric constraints preventing insertion across the Sc-alkyl bond. The ansa-scandocenes $(CH_3)_2Si[C_5(CH_3)_4]_2Sc(H)P(CH_3)_3$ (OpSc(H)PMe$_3$) and [*meso*-$(CH_3)_2Si[C_5H_3$-2-$C(CH_3)_3]_2ScH]_2$ ([DpScH]$_2$) selectively dimerize α-olefins in a head-to-tail fashion, and cyclize α,ω-diolefins,[13] indicating that the rate of β-H elimination from the dimeric scandium alkyl is greater than the rate of subsequent olefin insertions.

From the studies mentioned above and several other investigations a general consensus has emerged as to the various prerequisites for Ziegler-Natta catalysis. The requirements for polymerization activity, especially for α-olefins, appears to be a 14 electron metallocene alkyl fragment that has two empty frontier orbitals.[14] Current mechanistic thinking in regards to the mode of olefin insertion stems from the suggestions of Cossee and Arlman that the olefin inserts directly across the metal carbon bond, Figure 1.[15]

Figure 1. Cossee Arlman mechanism of olefin insertion.

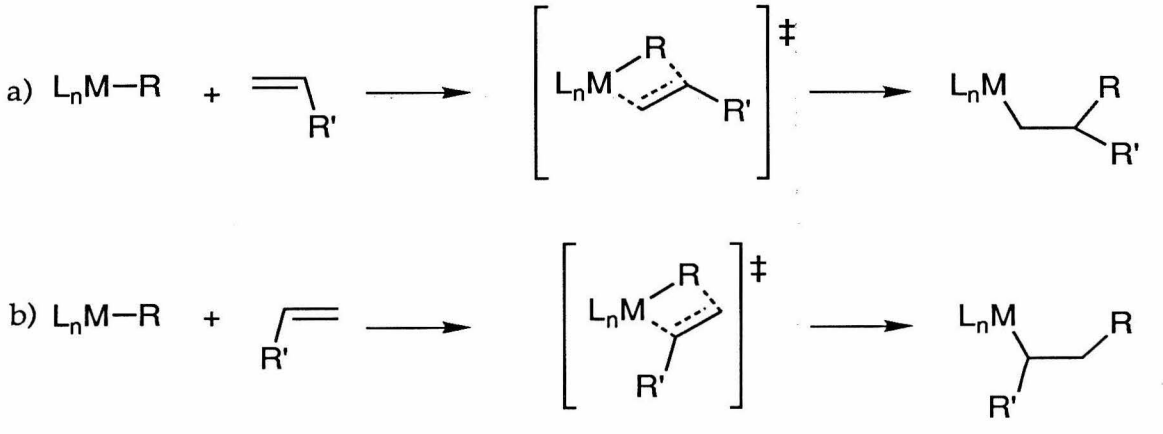


Brookhart and Green[16] have suggested that modification of an earlier proposal by Green[17] and Rooney[18] to include an α-agostic interaction in the transition state for olefin insertion may be necessary. Grubbs and co-workers noted no isotopic perturbation of stereochemistry in the products obtained from a stoichiometric cyclization experiment designed to probe the transition state for an α-agostic assistance in olefin insertion.[19] However, Bercaw and Piers demonstrated an isotopic perturbation of stereochemistry in the OpSc(H)PMe$_3$ catalyzed hydrocylcization of *trans,trans*-1,6-d_2-1,5-hexadiene to

d_2-methylcyclopentane.[20] Brintzinger and Krauledat have observed similar isotopic perturbations in the hydrodimerization of *trans*-d_1-1-hexene catalyzed by *rac*-ethylenebis-(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride/MAO.[21] The explanation offered for these observations is that an α-agostic interaction is present during the C-C bond formation for these systems. An extended Hückel calculation indicates that the α-agostic assistance should serve to lower the overall barrier to olefin insertion into a metal carbon bond by ~12 kcal/mol relative to the non α-agostic insertion.[22] These results indicate that while an α-agostic effect may assist olefin insertion across a metal alkyl bond, it is not a general requirement for C-C bond formation. The requirement for a 14 electron alkyl species for olefin polymerization is rationalized by the assumption that one empty orbital serves as the coordination site of the olefin and that the second may or may not be involved in an α-agostic interaction that serves to assist olefin insertion.

Unlike the case with ethylene, the insertion of propylene into a metal alkyl can, in principle, occur with two different regiochemical results. Insertion of the olefin can occur in a 1-2 fashion by placement of the metal at the primary position of the new alkyl complex, Figure 2a. The reverse, addition in a 2-1 fashion results in a secondary metal alkyl, Figure 2b.

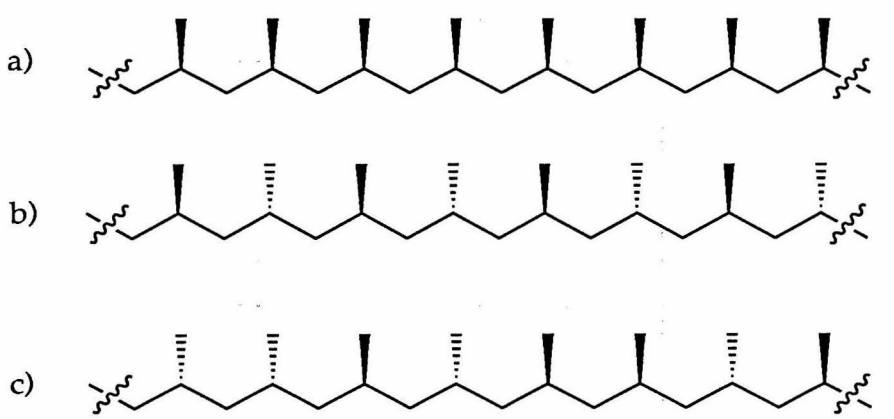
Figure 2. Regiochemistry of α-olefin insertion, a) 1-2 and b) 2-1.



Both modes of insertion have been observed for the heterogeneous systems of titanium and vanadium chlorides in combination with alkyl aluminum activators.[23] Investigation of the polymer end groups produced using metallocene catalysts shows that the mode of insertion is almost exclusively 1-2.[24]

In addition to the possible regiochemical outcomes, the insertion of propylene and higher α-olefins can result in several stereochemical outcomes. These possibilities arise because of the relative stereochemistry between the pseudochiral methine carbon atoms along the polymer backbone. Polypropylene with each methine carbon atom having the same relative stereochemistry, that is all pendant methyl groups directed toward the same side of the main chain, is termed *isotactic*, Figure 3a. Strict alternation of the orientation of the pendant methyl groups give the *syndiotactic* form of polypropylene, Figure 3b. A random orientation of the methyl groups results in *atactic* polypropylene, Figure 3c.

Figure 3. Different tacticities of polypropylene a) isotactic; b) syndiotactic; and c) atactic.

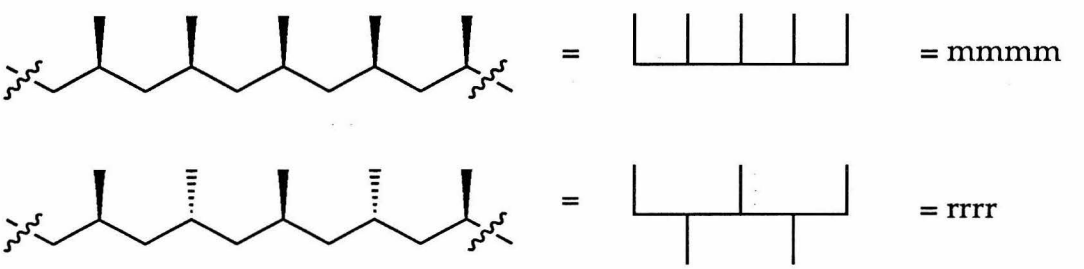


Isotactic polypropylene has found numerous industrial applications due to its high degree of crystallinity, and high melting point (T_m > 165 °C). Its high stiffness and tensile strength, as well as its ease of injection molding and extrusion make it ideally suited for numerous applications. The current production of several billion pounds per year in the United States alone attests to its incredible utility.[25] Syndiotactic polypropylene is slightly less

crystalline yet still retains a great deal of mechanical strength. Atactic polypropylene is an amorphous, waxy semi-solid and has little or no commercial value.

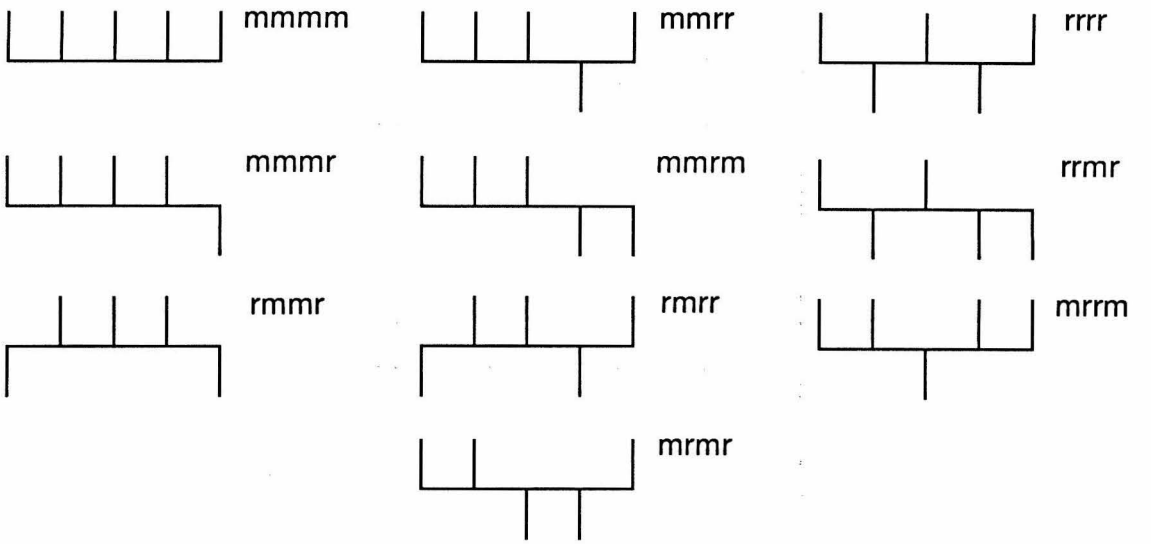
Distinguishing between the various tactic segments along a polymer sequence is readily accomplished using ^{13}C NMR spectroscopy.[26] The chemical shift of the various carbon atoms along a polymer chain are sensitive to the relative stereoconfiguration of the neighboring monomer units. The chemical shifts of the pendant methyl groups are found to be the most diagnostic resonances. An analysis of a five monomer sequence is possible since the chemical shift of the central methyl group is dependent upon the relative stereoconfigurations of the two monomer sequences directly preceding and following along the polymer chain. For simplicity, the various pentads are generally abbreviated using the convention shown in Figure 4.[27]

Figure 4. Stereochemical notation for polypropylene.



The polymer backbone is represented as a horizontal line and the relative orientations of the pendant methyl groups are shown as vertical lines. Each pentad is also given a four letter representation in which a lower case m designates a meso relationship between two adjacent chiral methine carbons. A lower case r is used to represent a racemo relationship between adjacent chiral methine carbons. The ten possible pentad sequences are shown in Figure 5.

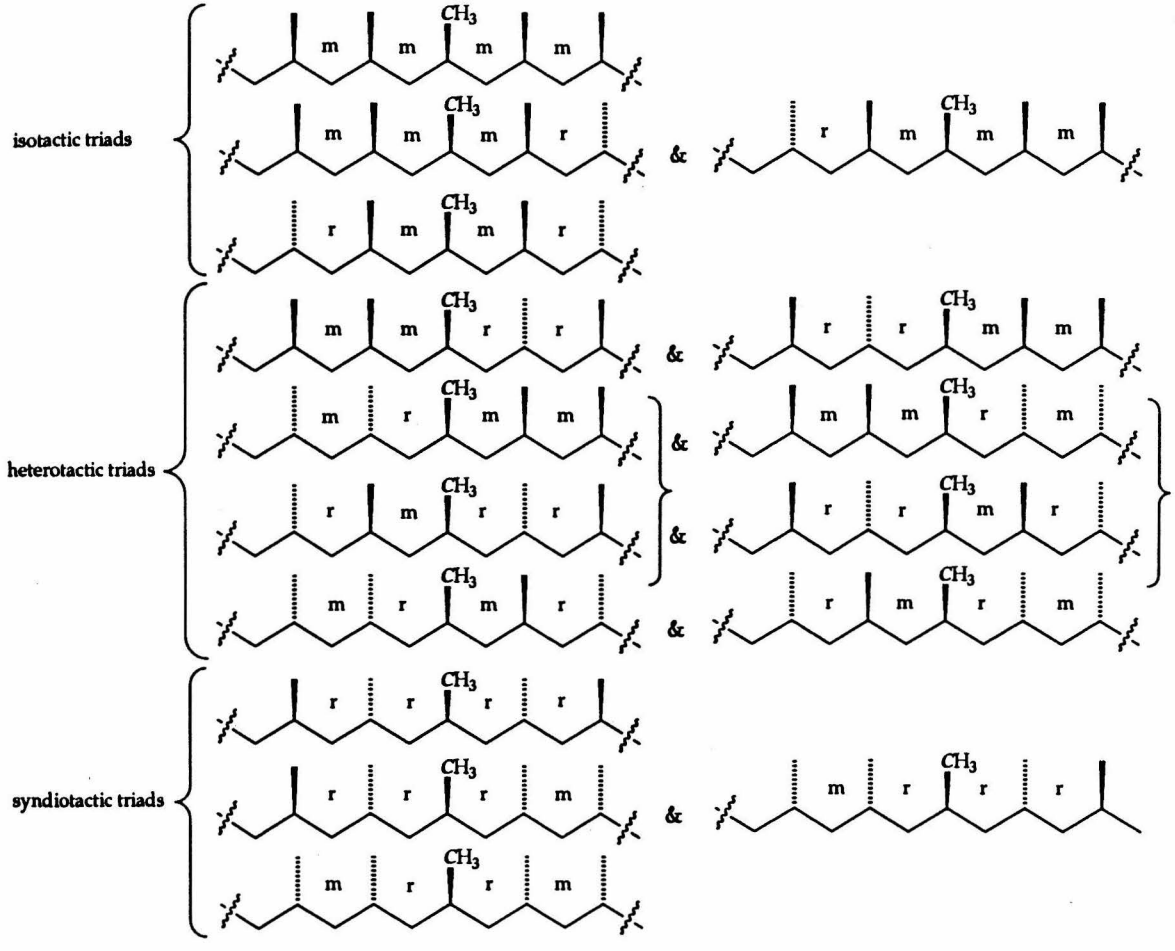
Figure 5. The ten possible pentad sequences for polypropylene.



In purely atactic polypropylene the probability that the next monomer inserted into the growing polymer chain will have either the same or opposite stereoconfiguration as the penultimate insertion is equal. Therefore, all ten pentad signals should appear as singlets in the methyl region of the proton decoupled ^{13}C NMR spectrum with their intensities related to the probability of their occurrence, Figure 6.[28]

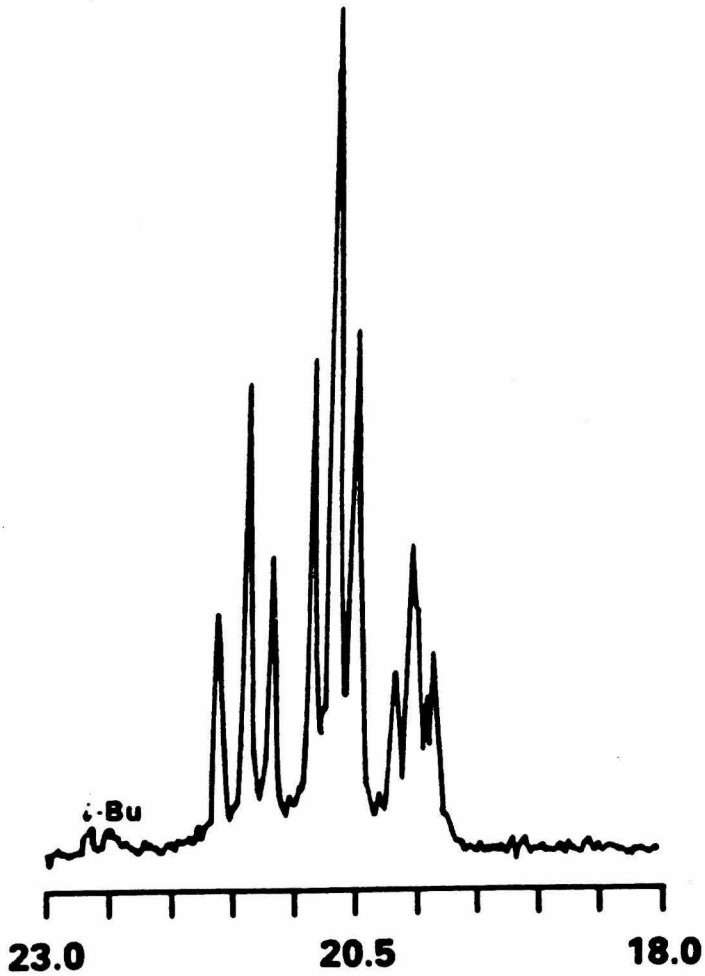
In reality only nine of the possible ten pentads can be observed as shown in Figure 7, since the mmrm and rmrr pentads are found to have chemical shifts that are not resolvable. The three regions of apparent 1:2:1 triplets are referred to as the isotactic, heterotactic and syndiotactic triads.

Figure 6. Pentad analysis probabilities for atatic polypropylene.

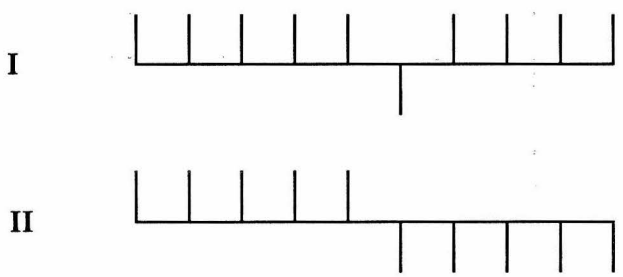


designation	relative intensity	$\delta(CH_3)$
mmmm	1	21.8
"mmmr"	2	21.5
rmmr	1	21.3
"mmrr"	2	21.0
"mrmm & rmrr"	4	20.8
"mrmr"	2	20.7
rrrr	1	20.3
"mrrr"	2	20.2
mrrm	1	20.0

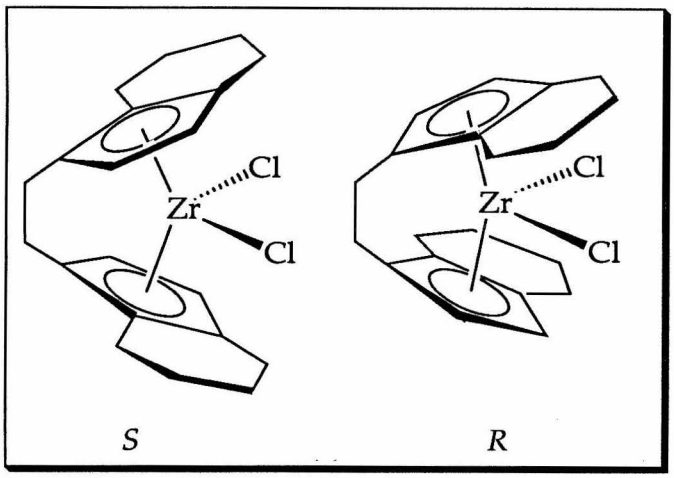
Figure 7. ^{13}C NMR spectrum of atactic polypropylene.



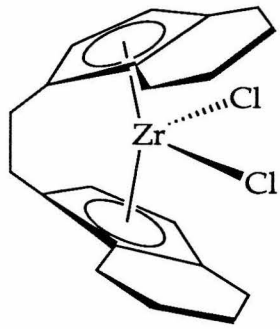
Stereoselection can be envisaged as arising from two different mechanisms. The first is enantiomorphic site control, wherein the ligand array about the transition metal catalyst is responsible for determining which prochiral face of the α-olefin inserts into the growing polymer chain.[29] In the chain end control mechanism, enantiofacial selection is dictated by the stereochemistry of the β-C of the last inserted monomer which direct the subsequent olefin insertion into the polymer chain.[30] Distinguishing between these two types of insertion control is conveniently determined by ^{13}C NMR spectroscopy. For enantiomophic site control an error that occurs in olefin insertion will immediately be corrected in the next insertion, whereas in a chain end control the error will continue along the chain. This leads to two different mistake sequences in a polymer chain, type **I** for enantiomorphic site control and type **II** for chain end control. The experimentally observed tacticity generally results from a combination of both chain end and enantiomorphic site control.[31]



The first reported homogeneous isospecific polymerization of propylene and 1-butene was reported using the C_2-symmetric ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium chloride (**racemic 1b**) in combination with methylalumoxane.[32] A remarkable feature of this system is that under certain conditions the activity is comparable or even surpasses the activity of the best heterogeneous "high mileage" catalysts. The regiochemistry of insertion was determined to be predominately 1-2. The resultant polymers were highly isotactic with evidence for enantiomorphic site control being implicated as the cause of the stereoregularity.



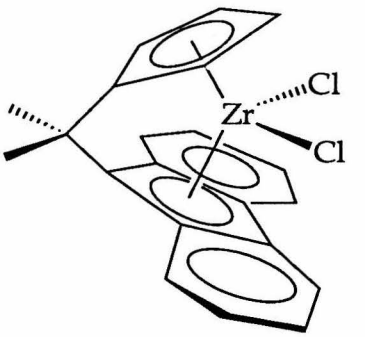
racemic 1b



meso 1b

The corresponding achiral meso derivative (**meso 1b**) was found to have much lower activity and produce atactic polypropylene.[33] These two results taken together clearly demonstrate that during activation of the metallocene dichlorides with MAO both tetrahydroindenyl rings remain attached to the metal center, and that isomerization does not occur. Removal of a single tetrahydroindenyl ring from either **racemic** or **meso 1b** would result in analogous structures that would presumably give polymers of similar microstructure.

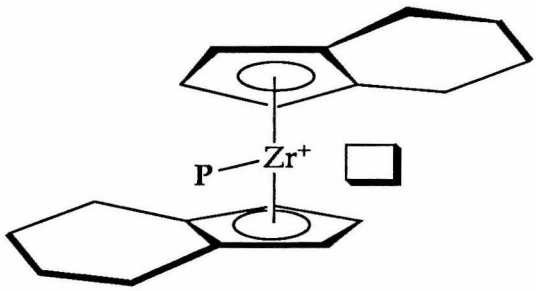
The synthesis of syndiotactic polypropylene has recently been accomplished using a homogeneous catalyst derived from the combination of isopropyl(cyclopentadienyl-1-fluorenyl)zirconium dichloride (**30**) and MAO.[34] This was one of the first reports of syndiotactic polymerization occurring at or above ambient temperature. The mode of insertion was found to be 1-2 and the resultant syndiospecificity was found to be produced through an enantiomorphic site control mechanism.



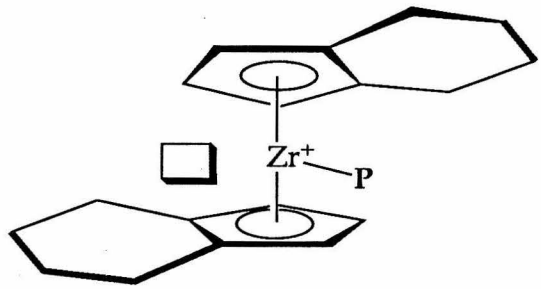
30

An explanation for the different tacticities observed for the polymers produced by **racemic 1b** and **30** is shown in Scheme 1. For insertion of propylene into the growing polymer chain (**P**) of the ionic complex **rac-31**, addition occurs in a 1-2 fashion. The insertion should take place at the open coordination site represented by the shaded box. Based on steric considerations, the olefin should approach with the methyl group pointed away from the six membered ring of the tetrahydroindenyl ligand.[35] By virtue of the overall C_2 symmetry of the complex the enantioface of insertion is identical regardless of whether olefin adds from the left or the right (**rac-31** = **rac-31'**). Thus insertion of an olefin into the growing polymer chain generates the same relative configuration at each methine carbon and formation of isotactic polypropylene results. For the cationic C_s symmetric complex **32** 1-2 olefin insertion with the propylene methyl group directed away from the six membered rings of the fluorenyl ligand results in insertion of different enantiofaces into the growing polymer chain. Complexes **32** and **32'** are enantiomers, and olefin insertion into **32** leads to formation of **32'** and vice versa. Thus, repeated insertions result in the generation of methine carbons with opposite relative stereocenters and, therefore, formation of syndiotactic polypropylene.

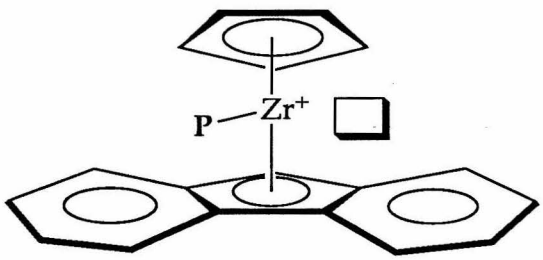
Scheme 1.



rac 31



rac 31'



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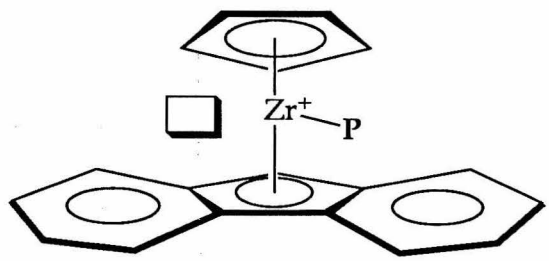


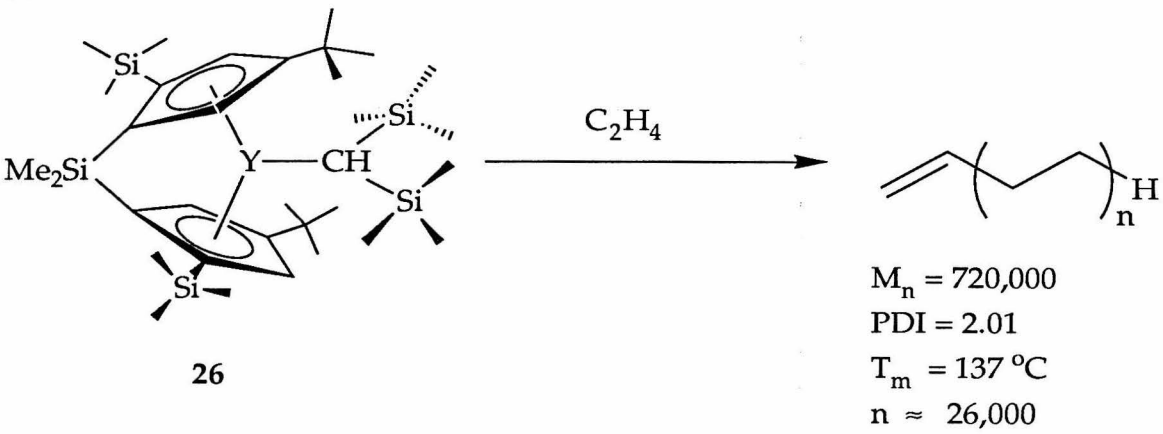
32'

With the apparent general requirement for olefin polymerization activity being a 14 electron alkyl as noted earlier. A series of investigations into the possibility that several of the yttrocene complexes reported in chapter 2 to catalyze the Ziegler-Natta polymerization of α-olefins was undertaken. With the high degree of isotacticity observed for polymers produced by complex **rac-1b** and other C_2 symmetric ansa-zirconocene dichlorides in conjunction with MAO it was further hoped that the resultant poly-α-olefins produced would possess a high degree of isotacticity.

Results and Discussion

The yttrium alkyl species $[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]YCH(Si(CH_3)_3)_2$, **26**, efficiently initiates ethylene polymerization. Solutions of **26** in methylcyclohexane were found to catalyze the rapid polymerization of ethylene to high molecular weight linear polyethylene. The physical data for the polyethylene produced is presented in Scheme 2.

Scheme 2.



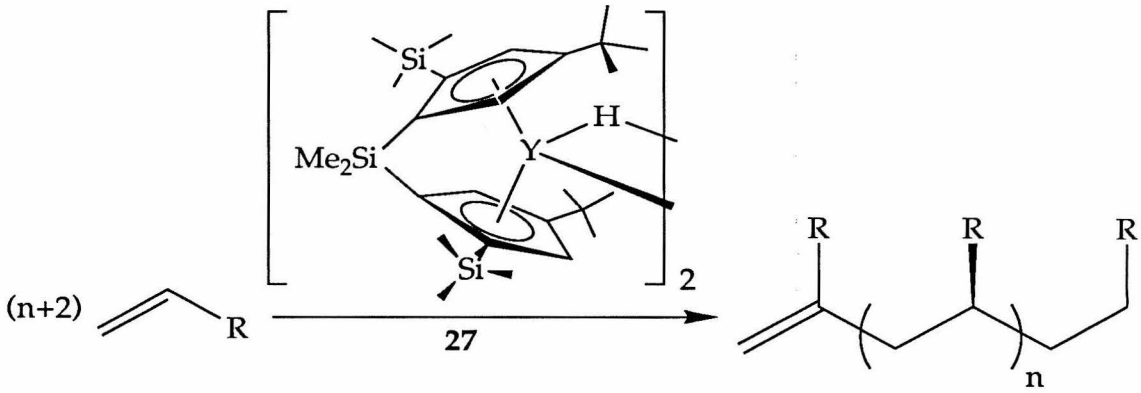
26

The overall yield of isolated polymer is only 50%, presumably due to mass transport problems during polymerization since the polymer almost immediately precipitates from solution. The average number of monomers per chain, (n= 26,000), is much higher than the starting monomer/catalyst ratio 3200:1. This discrepancy indicates that the rate of propagation is much greater than the rate of initiation; consequently, only a small fraction of **26** initiates ethylene polymerization. The exact mode of initiation remains uncertain; ethylene may insert directly across the Y-C σ bond of **26**, or perhaps σ bond metathesis of ethylene to form a BpY-vinyl species that could initiate polymerization is occurring.[36]

From a manufacturing standpoint very high molecular weight linear polyethylene has several desirable features, toughness and excellent chemical resistance are but two attractive properties. However, processing becomes more difficult as the molecular weight increases. The copolymerization of ethylene and 1-butene allows for the incorporation of ethyl side chains that disrupt crystalline packing forces and allows for easier processing while at the same time maintaining excellent mechanical properties. Copolymers of ethylene and 1-butene have been prepared using **26** as a catalyst. Polymerization of α-olefins is not observed in the presence of **26**. The large alkyl group, $-CH(Si(CH_3)_3)_2$, is apparently sufficiently bulky so as to preclude initiation of α-olefin polymerization.

Solutions of $[[(CH_3)_2Si(4\text{-}(CH_3)_3C\text{-}2\text{-}(CH_3)_3Si\text{-}C_5H_2)_2]YH]_2$, **27** ($[BpY\text{-}H]_2$), are found to slowly polymerize α-olefins to moderately high molecular weight polymers, Scheme 3. The physical characterization data for the polymers produced are shown in Table I.

Scheme 3.



R = CH_3; CH_2CH_3; $CH_2CH_2CH_3$; $CH_2CH_2CH_2CH_3$

Table I. Physical data for poly-α-olefins prepared with **27.**

Polymer	M_n	PDI	DP[c]	T_m °C
polypropylene	4,200	2.32[a]	100	156
poly-1-butene	11,000	1.83[b]	187	109
poly-1-pentene	20,000	1.99[b]	284	73
poly-1-hexene	24,000	1.75[b]	287	<25

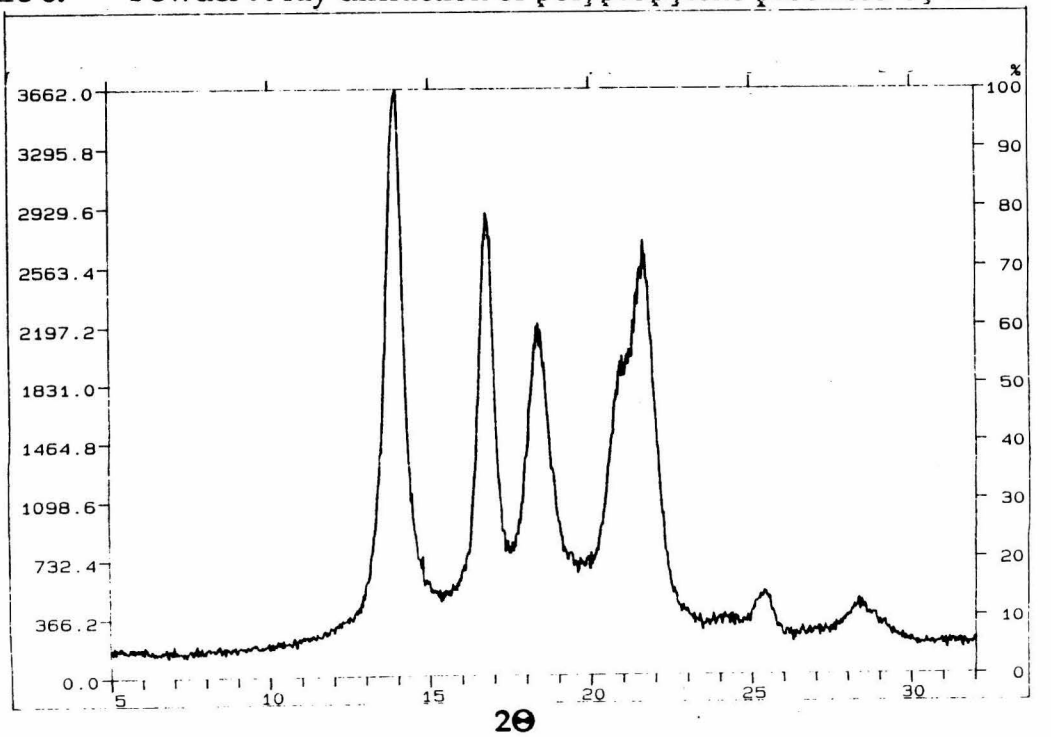
a) GPC versus authentic molecular weight polypropylene. b) GPC values versus narrow molecular weight polystyrene standards. c) Average degree of polymerization.

The polymerization is quite slow, presumably due to the inactivity of the 16 electron dimeric hydride complex **27**. A 14 electron hydride or alkyl derivative is probably required for α-olefin polymerization.[37] Faster polymerization rates can be achieved by in situ generation of the 14 electron monomeric hydride species "BpY-H" by hydrogenolysis of **26** in the presence of a large excess of α-olefin. The results obtained for each of the poly-α-olefins produced will be discussed in turn.

Polypropylene

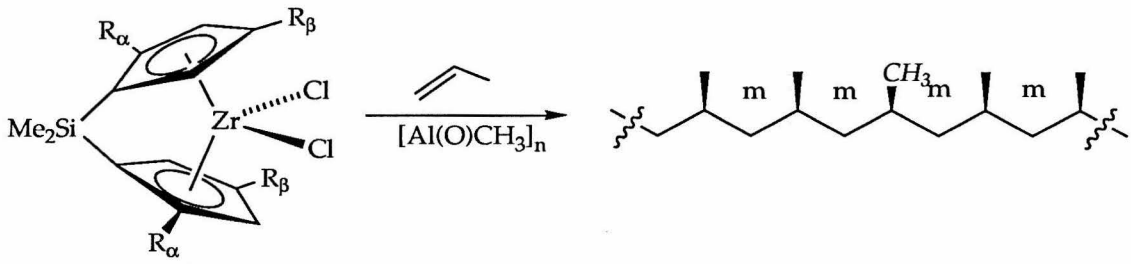
Polymerization of solutions of propylene in methylcyclohexane (1:3 v/v) proceed smoothly using **27** as the catalyst. As the reaction progresses, polypropylene is observed to precipitate from solution. After the reaction was quenched with acidic methanol to remove the catalyst, the solid was isolated by filtration. Drying the solid in vacuo generally gave a 50-75% yield of polymer based on monomer consumption. The results of a detailed ^{13}C NMR pentad analysis of the unfractionated polypropylene reveals that the mmmm resonance accounts for >99% of the methyl resonances present. Chain end analysis by ^{1}H NMR shows both vinyl and vinylidene end groups indicative of both β-H[38] and β-methyl elimination[39] pathways for chain termination. Infrared analysis of a thin film of the polymer indicates the isotacticity index to be 96.9%.[40] Analysis of the resultant polymer by powder X-ray diffraction methods indicate that the polypropylene is highly crystalline, Figure 8, and exists in a monoclinic unit cell with two enantiomorphous helices facing one another, (modification α).[41]

Figure 8. Powder X-ray diffraction of polypropylene produced by **27**.



Comparison with the polypropylenes produced by zirconocene **7**, Scheme 4, that has a similar ansa-ligation to the Bp ligand reveals the importance of alkyl substitution about the cyclopentadienyl rings.[42] The presence of a methyl group at the R_α position in **7e, 7f** was found to decrease the number of 1-3 misinsertions from 1.5 to 0.6%. 1-3 Misinsertions are the net result of a 2,1 misinsertion followed by rapid isomerization of the secondary alkyl to a primary zirconocene alkyl.[43] The corresponding percentage of 1,3 misinsertions found for the polypropylene produced by **27** was <0.1%. The tremendous importance of the *tert*-butyl group is attested to by the precipitous drop in isotacticity found upon replacement of the *tert*-butyl group with the less sterically demanding *iso*-propyl group, cf. **7e, 7f** Table II.

Scheme 4.



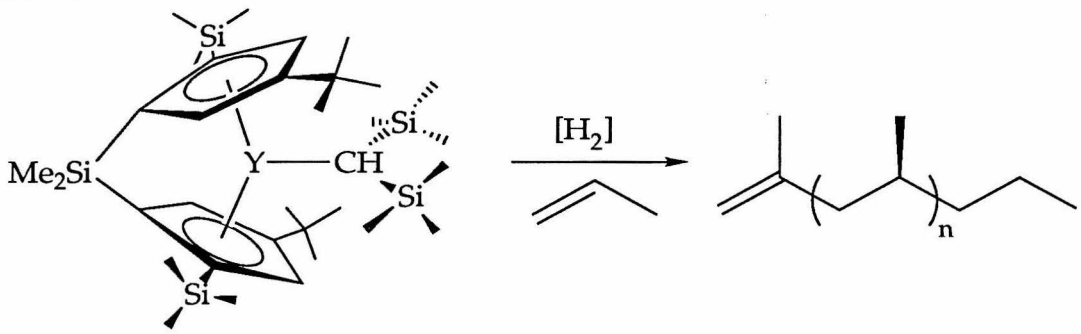
rac **7**

Table II. ^{13}C NMR pentad analysis of polypropylene produce by **7**.

	R_α	R_β	% mmmm
7a	H	$C(CH_3)_3$	77
7e	CH_3	$C(CH_3)_3$	94
7f	CH_3	$CH(CH_3)_2$	73

Increased rates of polymerization can be achieved by the in situ hydrogenolysis of **26** in the presence of propylene. Hydrogenation of α-olefin solutions of **26**, monomer/catalysts >3000, presumably results in initial formation of a 14 electron monomeric hydride complex, "BpY-H", which rapidly initiates polymerization, Scheme 5. For both propylene and 1-butene polymerizations polymer precipitation was apparent almost immediately upon hydrogenation. The results of a study that measured the effect of temperature on the polymerization of propylene is presented in Table III.

Scheme 5.



26

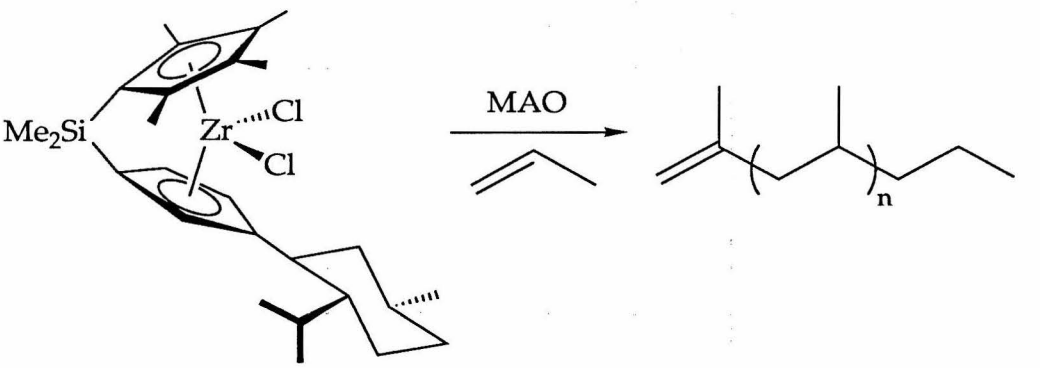
Table III. Molecular weight data and activity for polypropylene produced by in situ hydrogenolysis of **26**.

T_p (°C)[a]	M_n	PDI[b]	DP	T_m (°C)	Activity[c]
50	2200	1.7	53	142	709
24	7000	2.6	167	153	1760
6	3800	3.4	90	141	305

a) Polymerization temperature ± 2 °C. b) GPC data versus authentic molecular weight polypropylene. c) [g Polymer]/[(mol Y)h]

While the data presented in Table III display considerable scatter due to experimental difficulties, several features are worthy of note. The use of H_2 for the in situ generation of "BpY-H" does result in an increased rate of initiation, however, the rate of hydrogenation of **26** is slower than that of hydrogenation of the growing alkyl chains. This results in the production of low molecular weight oligomers, the GPC traces for these polymer samples show bimodal distributions with a small bias towards short chain oligomers. While the hydride dimer is stable at elevated temperatures the thermal stability of a putative hydride monomer or growing alkyl chain is unknown.

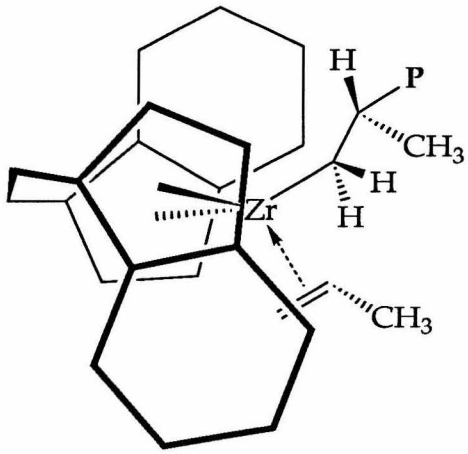
A recent report by Marks and co-workers reveals that a C_2 symmetric ligand array is not a direct prerequisite for isotactic poly-α-olefin formation. A series of ansa-zirconocenes were prepared in which a menthyl or neomethyl substituent was attached at the 3 position to one cyclopentadienyl ring. Activation of the zirconocenes with MAO produced catalysts capable of polymerizing propylene. However, isotacticities comparable to those reported here could only be achieved by conducting the polymerizations at -40 °C.[44]



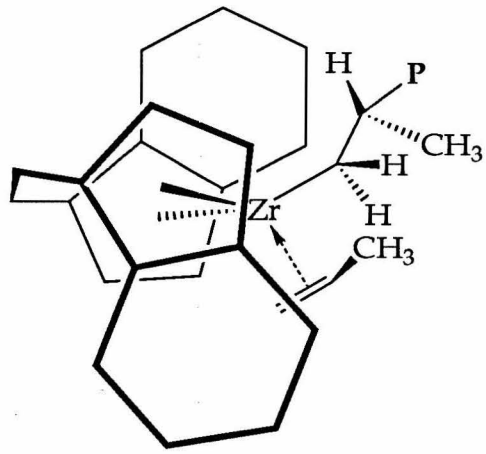
Numerous investigations, both experimental and theoretical, have been undertaken to elucidate the nature of the transition state of α-olefin insertion, the step that determines the stereochemical outcome, into the growing polymer chain. Olefin hydrogenation and oligomerization studies have been conducted using optically pure (*R*) and (*S*)-(ethylenebis(4,5,6,7-tetrahydroindenyl)zirconocenes and methylalumoxane.[45] These studies indicate that the most probable transition

state for olefin insertion into the metal-alkyl bond occurs with the alkyl substituent of the α-olefin directed away from the tetrahydroindenyl ring. Using this proposed transition state geometry, Scheme 6, molecular mechanics calculations derived the energy difference between insertion leading to isotactic chain extension, **III**, to be 3-6 kcal/mol lower in energy than the insertion leading to a syndiotactic defect, **IV**.[46]

Scheme 6.



III



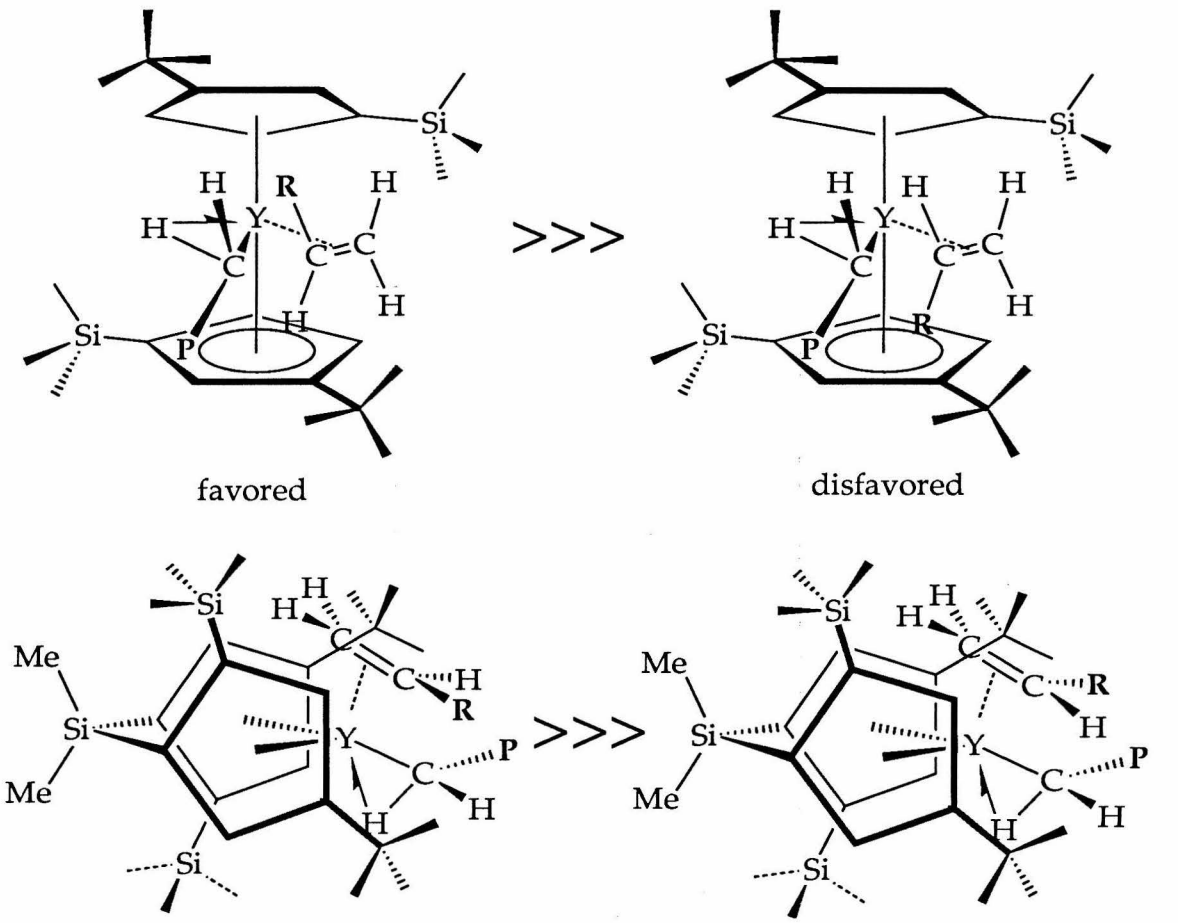
IV

One important feature that has been neglected in zirconocene alkyl cation polymerizations is the role of the methylalumoxane counterion. Experimental studies are generally conducted in benzene or toluene, and the degree of ion pairing between zirconocene alkyl cation and the MAO anion may play a crucial role in determining the tacticity of the resultant polymer.[47]

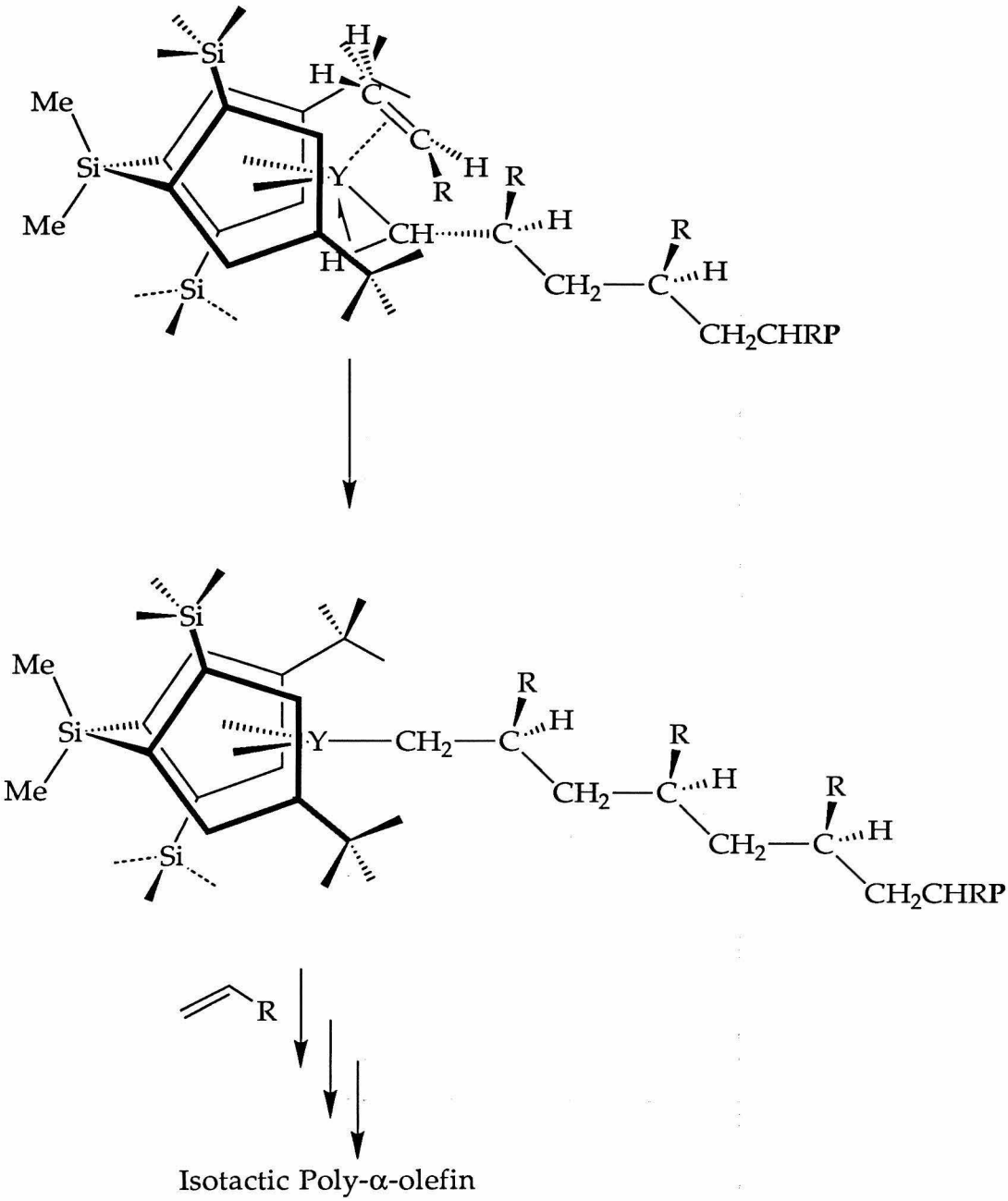
Our current mechanistic thinking as to the geometric constraints of the transition state for α-olefin insertion parallel those presented above. However, due to the neutral nature of the BpY catalysts no adjustment for a counterion is required. Preliminary investigations in collaboration with T. Herzog analogous to those conducted by Piers and Bercaw on 1,6-d_2-1,5-hexadiene hydrocyclization using **26** indicate an isotopic perturbation of stereochemistry in the resultant methylcyclopentane-d_2 products. This result suggests that an α-agostic effect may operate during C-C bond formation,[48] but the result is not definitive.

The presumed transition state geometry is shown in Scheme 7. Two views each are shown for the favored (left) and disfavored transition states (right). The preferred enantioface for propylene insertion is dictated by approach of the olefin such that the methyl group is pointed away from the *tert*-butyl group of the ligand, as well as in a transoid arrangement with the growing polymer chain. The size difference between the two distal substituents on the cyclopentadienyl ring, H versus *tert*-butyl, may permit an avenue of approach ideally suited for α-olefin insertion. The possible role of an α-agostic interaction may be two-fold. First, such an interaction may lower the transition energy required for olefin insertion as suggested by the calculations of Brintzinger. Second, adoption of an α-agostic interaction serves to orient the two remaining substituents on the α-C toward the cyclopentadienyl rings. The preferred orientation should be such that the smaller hydrogen atom is directed toward the *tert*-butyl group of the upper ring, while the larger polymer fragment, **P**, is pointed into the open region between the *tert*-butyl and trimethylsilyl groups of the lower ring. The overall substitution pattern of the Bp ligand in conjunction with the adoption of an α-agostic interaction may provide a well defined steric environment for α-olefin insertion. Regardless of whether or not there is an α-agostic effect present, the specific substitution pattern of the Bp ligand is expected to effectively discriminate between olefin enantiofaces. Repeated isospecific insertions are expected to yield highly isotactic polypropylene as shown in Scheme 8.

Scheme 7.



Scheme 8.


Me
Si
Me
Si
H
H
C
C
H
R
R
Y
CH
H
C
H
R
CH2
C
H
R
CH2CHRP
Si
Me
Si
Me
Si
Y
CH2
C
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R
CH2
C
H
R
CH2
C
H
R
CH2CHRP
R
Isotactic Poly-α-olefin

Poly-1-butene

Polymerization of neat samples of 1-butene with either **27** or by in situ generation of "BpY-H" gave polymers with a very high degree of isotacticity. The polymer produced by the hydride dimer was found to have a higher molecular weight and a narrower polydispersity (M_n 10900, PDI 1.84) than the polymer produced by the in situ method (M_n 1850, PDI 4.44). The melt transition temperature was also found to be higher for the longer polymer sample, 109 °C versus 94 °C. The high degree of isotacticity is readily apparent by inspection of the ^1H and ^{13}C NMR spectra of the high molecular weight sample, Figure 9. Analysis of a thin film, by IR spectroscopy revealed that the poly-1-butene exists in the more stable of the two possible helical forms.[49] The helical form with three repeat units per turn is known to have greater tensile strength and a higher melting point than the less stable form with 11 monomer units per two helical turns.

Poly-1-pentene

1-Pentene is polymerized by **27** over the period of several days to a polymer of moderately high molecular weight. The overall yield of polymer corresponds to approximately 50% of the monomer being consumed. Unlike the hard and brittle polypropylene and poly-1-butene produced, the poly-1-pentene is a much softer, waxy material. ^1H NMR analysis of the polymer reveals vinyl end groups indicating chain termination by β-H elimination. ^{13}C NMR analysis of the polymer indicates that the degree of isotacticity is extremely high, Figure 10. Assignment of the various pentad chemical shifts for poly-1-pentene have recently been reported.[50] The C^3 methylene resonances for the poly-1-pentene produced by **27**, and a sample of poly-1-pentene produced by a classical heterogeneous Ziegler-Natta catalyst system are presented in Figure 11. The reported isotacticity of the poly-1-pentene produced by the heterogeneous catalysts is only 51% mmmm, comparison with the poly-1-pentene produced by **27** shows the isotacticity to be at least 95% mmmm if not higher.

Poly-1-hexene

1-Hexene is polymerized in excellent yield (~95%) by either initiation system mentioned previously. The resulting polymers were very viscous semi-solids with a melt transition below 30 °C. ^{13}C NMR analysis reveals only six resonances for each type of carbon atom along the polymer chain as expected for highly isotactic poly-1-hexene, Figure 12.

Figure 9. a) ^{1}H NMR spectrum (400 MHz) (*o*-dichlorobenzene/benzene-d_6, 9:1 v/v, 100 °C) with tentative assignment of resonances. b) ^{13}C NMR spectrum (100 MHz) (*o*-dichlorobenzene/benzene-d_6, 9:1 v/v, 100 °C) obtained by polymerization of neat 1-butene at 25 °C with **27**.

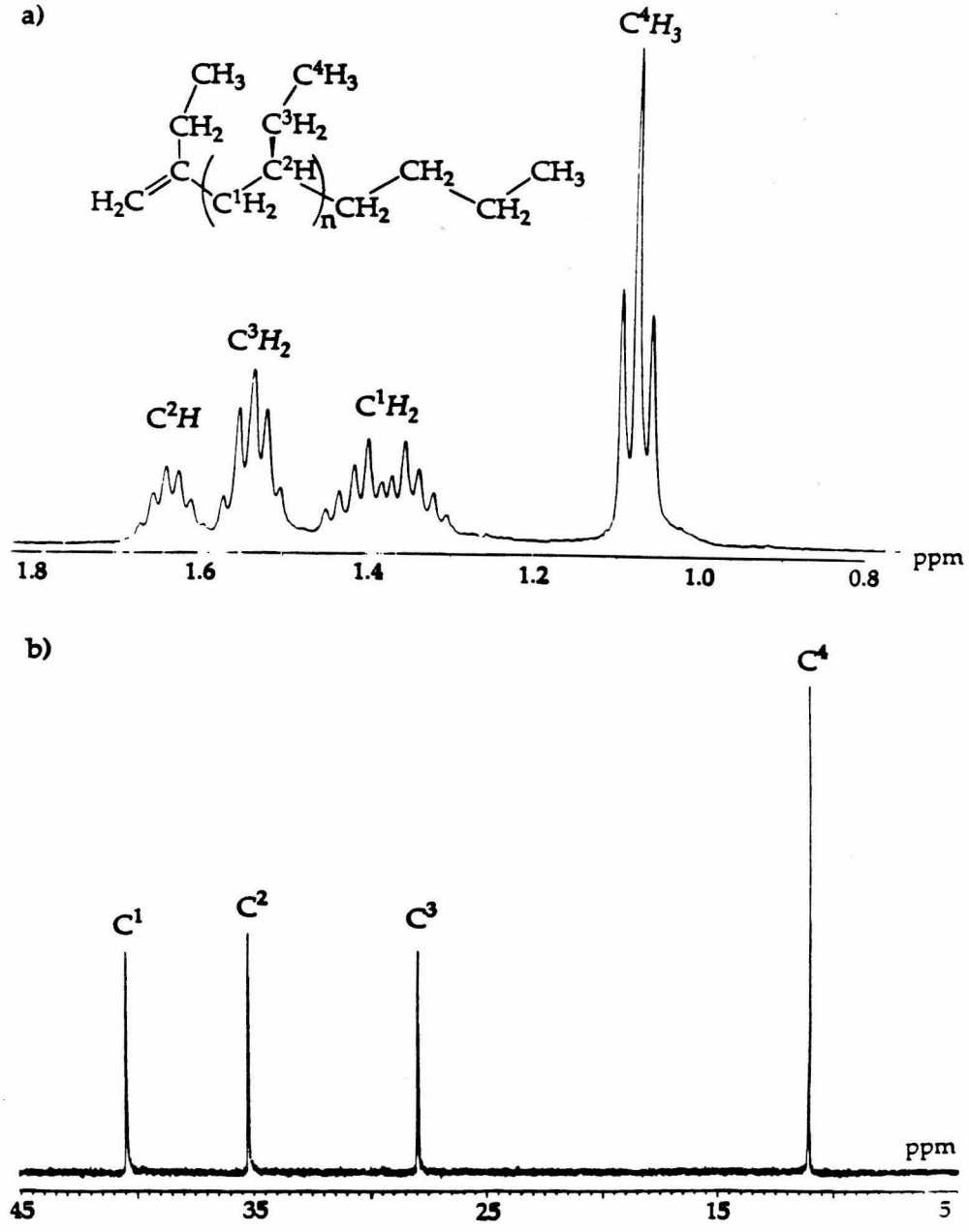


Figure 10. ^{13}C NMR spectrum (100 MHz) (*o*-dichlorobenzene/ benzene-d_6, 9:1 v/v, 25 °C) obtained by polymerization of neat 1-pentene at 25 °C with **27**.

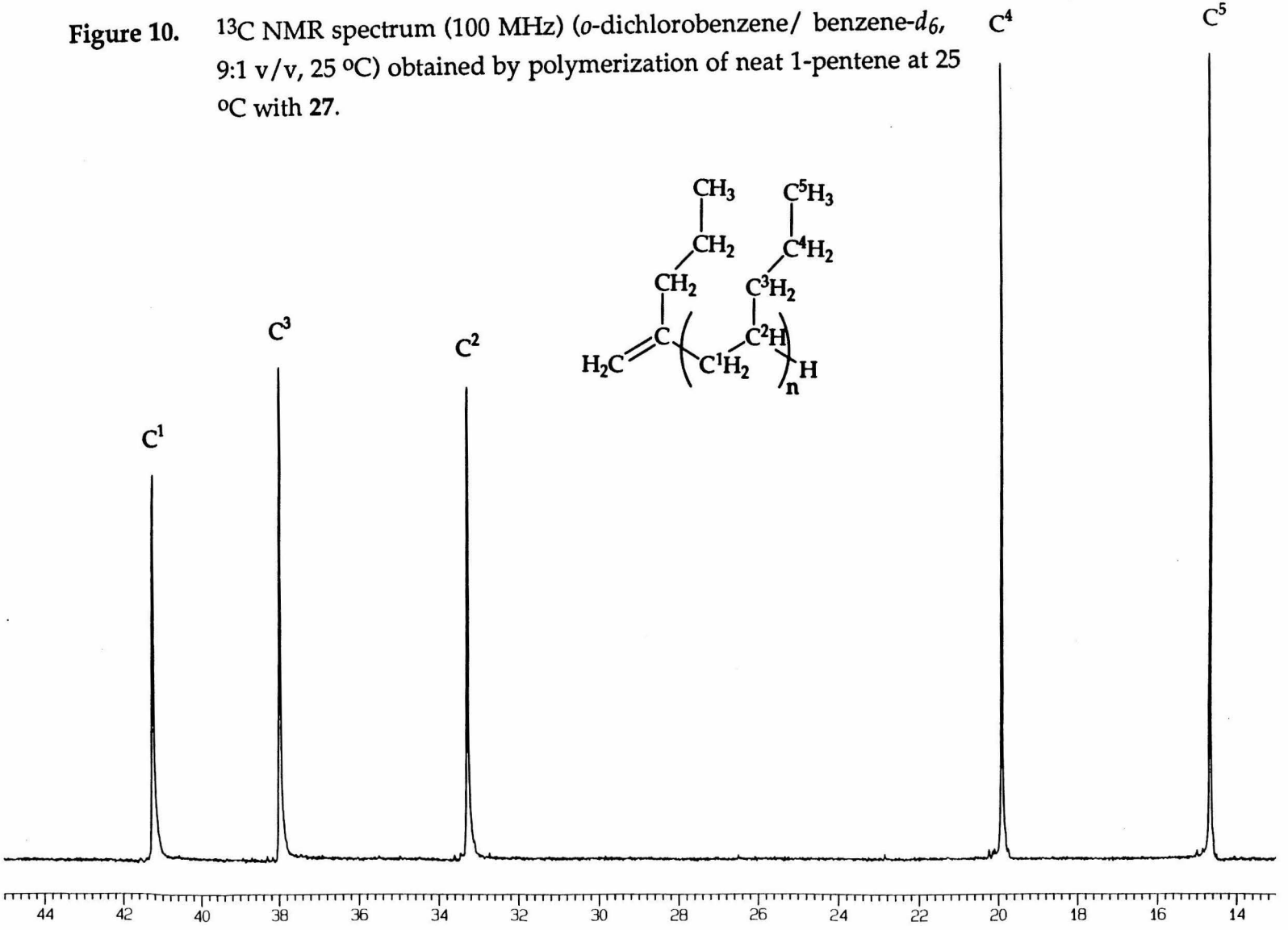


Figure 11. Expansion of resonance C3 for poly-1-pentene prepared by **27** (left) and $TiCl_3/MgCl_2/SiO_2/Al(CH_2CH_3)_3$ (right).

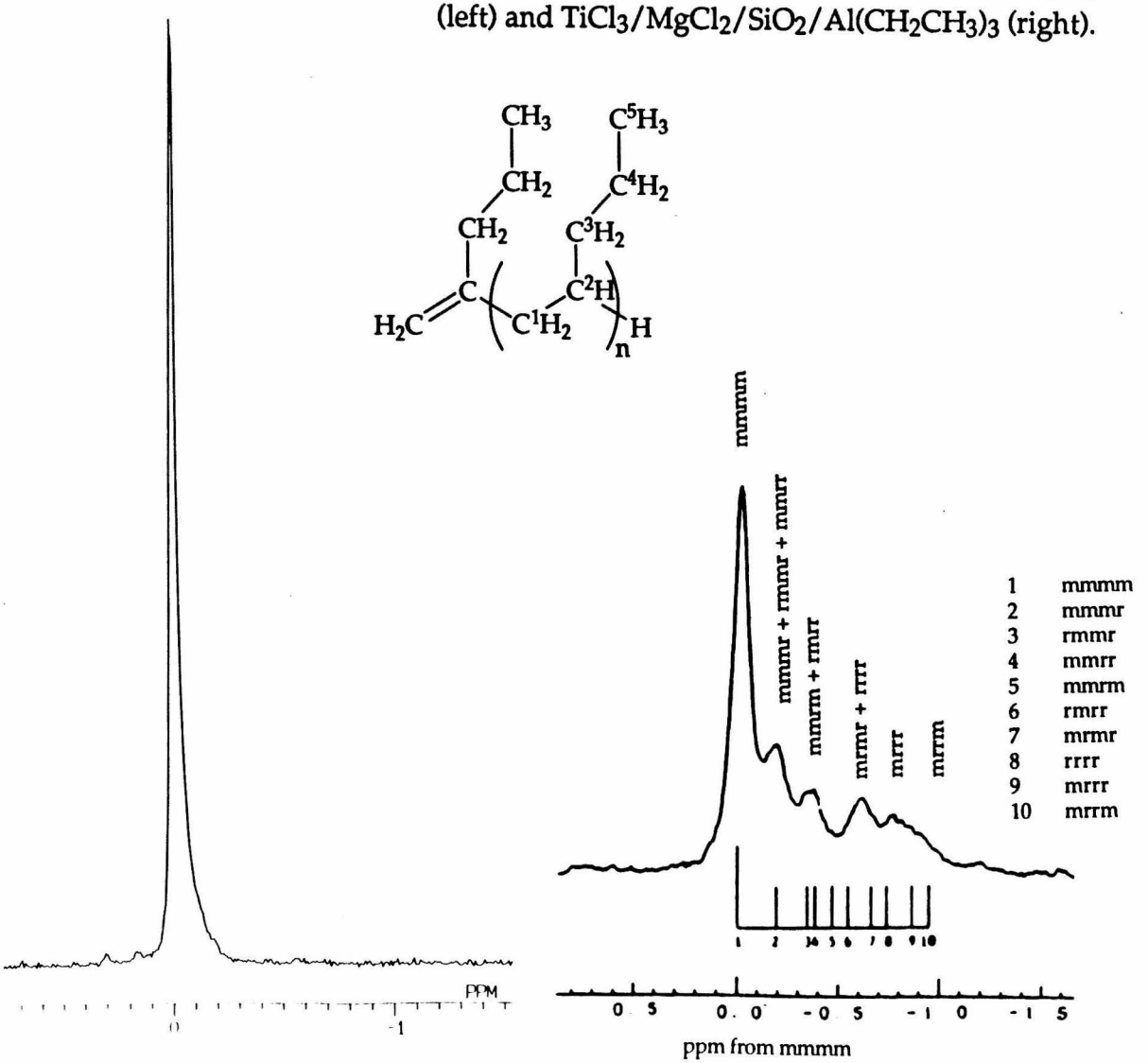
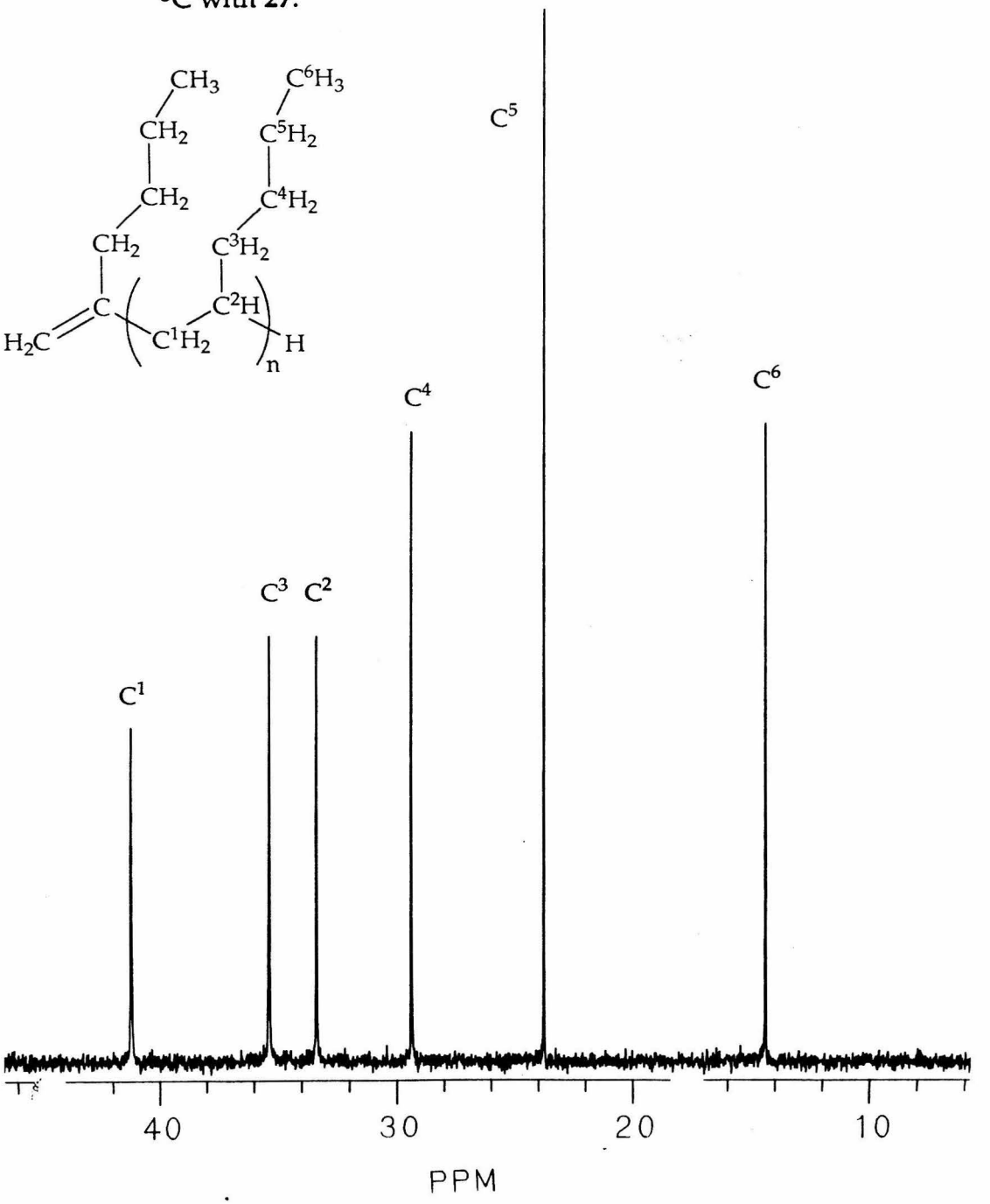


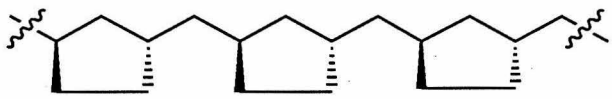
Figure 12. ^{13}C NMR spectrum (100 MHz) (*o*-dichlorobenzene/ benzene-d_6, 9:1 v/v, 25 °C) obtained by polymerization of neat 1-hexene at 25 °C with **27**.



1,5-Hexadiene

Recently Waymouth and co-workers have investigated several unique features of poly(methylenecyclopentane), a polymer first prepared by Marvel and Stille.[51] In a preliminary account, trans selectivity was noted for 1,5-hexadiene cyclopolymerizations using Cp_2ZrCl_2 in conjunction with MAO as the catalyst system. Use of the more sterically demanding pentamethylcyclopentadienyl analog ($Cp^*_2ZrCl_2$) gave predominantly *cis*-poly(methylenecyclopentane).[52] Use of the optically active (*R*)-ethylenebis(tetrahydroindenyl)zirconium (*R*) binaphtholate and MAO was found to cyclopolymerize 1,5-hexadiene to produce an optically active *trans*-poly(methylenecyclopentane), Figure 13.[53] The two requirements for polymer chirality are isotacticity of the main chain, and trans-fused 5 membered rings. These results demonstrated unambiguously that chiral and optically active polymers can be prepared starting from achiral monomers by judicious choice of catalyst.

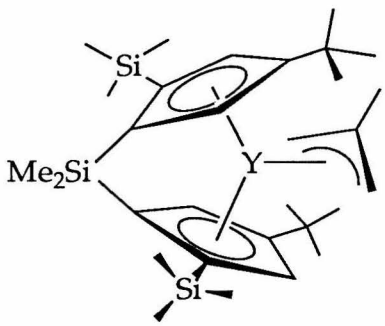
Figure 13. Trans-diisotactic poly(methylenecyclopentane).



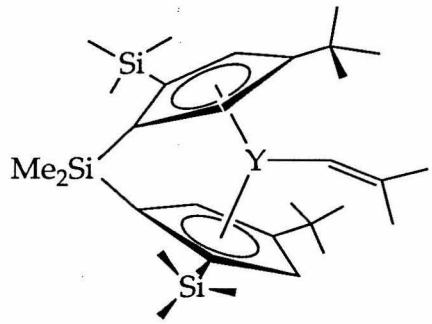
Neat 1,5-hexadiene is readily cyclopolymerized by addition of **27**. Analysis of the product reveals a polymer of moderate molecular weight (M_n 17,000) and broad unimodal molecular weight distribution (PDI 3.2 versus polystyrene standards). Little or no crosslinking via pendant vinyl side chains, which would result from incomplete cyclization, is observed. ^{13}C NMR analysis of the poly(methylenecyclopentane) shows the 5-membered rings to be predominantly trans-fused.[54] Detailed triad analysis was not possible due to the limited spectral resolution. The high isotacticities observed in the polymerization of various α-olefins (vide supra), and the observed trans ring formations suggest that **27** or closely related derivatives might serve as possible enantioselective cyclopolymerization catalysts provided that suitable resolution methods for this class of ansa-metallocene can be devised.

Gem-disubstituted Olefins

The sluggishness or complete inability of geminally disubstituted olefins to undergo Ziegler-Natta polymerization prompted us to investigate whether or not a single insertion across BpY-H might be observed. Furthermore we hoped that the alkyl derivatives if formed could serve as an initiator for α-olefin polymerizations. Addition of isobutylene to **27** shows no reaction at room temperature. Heating the sample to 80 °C cleanly afforded a single organometallic species identified (^{1}H NMR) as the 2-methylallyl complex **33**, resulting from σ bond metathesis of an allylic methyl group.



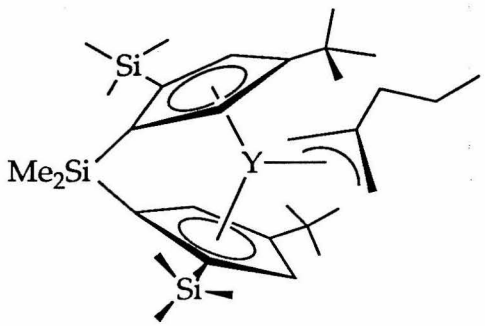
33



34

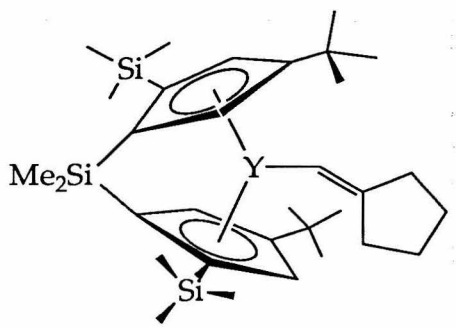
Whether the product is the result of direct allylic C-H σ bond metathesis, or results from either intra- or intermolecular rearrangement of the vinylic species **34** is unknown. The vinylic species is a logical intermediate given the greater propensity of sp^2-hybridized C-H bonds to undergo σ bond metathesis relative to sp^3-hybridized C-H bonds.[55] Isomerization of the allyl (η^3-η^1-η^3) is slow on the ^{1}H NMR timescale, as indicated by the lack of overall C_2 symmetry of the Bp ligand array.

The reaction of 2-methyl-1-pentene and **27** once again proceeds with allylic C-H bond activation to ultimately yield the allyl species **35**. The product was found to be almost entirely the result of σ bond metathesis with the less sterically hindered C-H bonds of the 2-methyl group. As with the product of the analogous reaction with isobutylene, **35** undergoes allyl isomerization only slowly, (^{1}H NMR).



35

Addition of methylenecyclopentane to **27** results in little or no reaction at room temperature. After heating at 80 °C for 6 h a new C_2 symmetric product is formed. Removal of the reaction volatiles in vacuo followed by re-examination of the organometallic species indicates that the product is presumably the result of vinylic C-H bond activation **36** (^{1}H NMR).

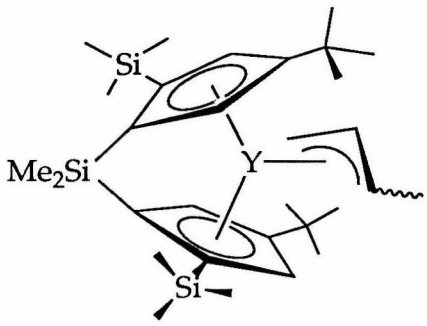


36

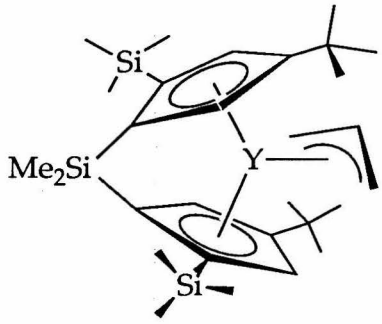
Addition of 10 equivalents of 1-pentene to the **36** results in oligomerization. However, only a small fraction of the metal centers catalyze the

oligomerization, as ~90% of **36** is still present after all the 1-pentene has been consumed.

The reaction of 1,3-butadiene and allene with **27** both require rather forcing conditions for formation of the crotyl **37**, and allyl species **38**, again allylic rearrangement is slow on the ^{1}H NMR time scale.



37



38

Conclusions

We have realized several of our goals. The alkyl derivative **26** is an excellent initiator for ethylene polymerization. Most gratifyingly, the dimeric hydride species **27**, and the putative monomeric hydride generated via hydrogenolysis of **26** are the first single component *iso-specific* polymerization catalysts. The high iso-specificities of the resultant poly-α-olefins presumably result from subtle steric factors exerted by the ligand substituents; thus the ligand array dictates which of the two prochiral enantiofaces of the incoming α-olefin inserts. The enantiofacial selection is remarkably high, even when distinguishing between such subtle steric differences as H versus CH_3. This discrimination is remarkably efficient such that isotacticity of the polypropylene produced is greater than 99% mmmm. Whether or not an α-agostic effect operates during polymerization has yet to be determined. The single component nature of this α-olefin polymerization catalyst should provide an unprecedented opportunity for a detailed investigation into the rate of olefin insertion in an actual iso-specific polymerization system. Finally, the high fidelity of olefin insertion into the yttrium alkyl bond suggest that if suitable resolution methods can be discovered optically active derivatives of **26** or **27** may prove to be useful catalysts for enantioselective transformations.

Experimental Section

General Considerations. Complexes **26** and **27** were prepared as described in Chapter 2. Olefins were dried over CaH_2, $LiAlH_4$ or titanocene.[56] Polymerizations of ethylene and propylene were conducted using solutions of the appropriate olefin in methylcyclohexane (1:3 -1:4 v/v). **Caution!** Polymerizations should never be conducted in glass reaction vessels on a neat sample of ethylene or propylene as the olefin vapor pressures are too great to be safely contained. Polymerizations of 1-butene, 1-pentene and 1-hexene were conducted on neat samples with the concentrations being; 1-butene 11.4 M, 1-pentene 9.12 M, and 1-hexene 8.00 M.

Instrumentation. Molecular weight distribution and melt transition temperature measurements for all polymer samples were performed at the Exxon Chemical Company Polymer Research Center in Baytown Texas. Molecular weight distributions were obtained using Gel Permeation Chromatography (GPC) on a Water model 150C chromatograph at 145 °C. Three Shodex mix bed columns were used. The solvent was 1,2,4-trichlorobenzene at a flow rate of 1 ml/minute. The system was calibrated using narrow molecular weight polystyrene standards. For polypropylene, a universal calibration with the appropriate Mark-Houwink constants was used to calculate molecular weights. For all other polymer samples the polystyrene calibration was used. Melt transition temperatures (T_m) were measured on a Du Pont 9900 Differential Scanning Calorimeter. The values reported are those obtained upon second melting after first annealing the sample by heating from room temperature to 200 °C at a rate of 10 °C/minute. The sample were held at 200 °C for 5 minutes then cooled at a rate of -10 °C/minute. The values reported are the minimum from the endotherm recorded during the second heating cycle (10 °C/minute). ^1H and ^{13}C NMR spectra were recorded on either a JEOL GX-400 (400 MHz ^1H, 100 MHz ^{13}C) or a General Electric QE-300 (300 MHz ^1H, 75 MHz ^{13}C) spectrometer. Delay times of 3-5 seconds were used when recording ^{13}C spectra. Polymer samples were run as 10 wt% solutions in either 1,2-$C_6D_4Cl_2$ or C_6D_6/1,2-$C_6H_4Cl_2$ (1:9 v/v). Powder X-ray diffractions were performed on a

Scintag XDS 2000 diffractometer utilizing Cu Kα radiation. Samples were scanned from 5° to 32° in 2Θ at a scan rate of 2°/min.

Polymerizations were conducted in thick walled glass reaction vessels (bombs) equipped with Kontes valve seals. Utmost care was taken to ensure that the olefins used were of the highest possible purity. Representative examples of polymerizations are presented below.

Polyethylene. A thick walled reaction vessel was charged with **26** (15.2 mg, 22 μmol) and evacuated. A second thick walled reaction vessel was charged with titanocene and 10.0 mL of methylcyclohexane. Ethylene (2.0 g, 71.3 mmol, 3200 equiv.) was condensed onto the titanocene at -196 °C. The resulting black solution of ethylene/methylcyclohexane was allowed to warm to room temperature with stirring. **Caution!** While no difficulties were encountered in handling solutions of ethylene/methylcyclohexane, extreme care should be exercised when working with solutions whose vapor pressure is greater than 1 atmosphere. Adequate shielding must always be employed when working with such solutions. The ethylene/methylcyclohexane solution was cooled to -78 °C and trap-to-trap distilled into the cold (-196 °C) reaction vessel containing **26**. The reaction was initially warmed to -78 °C to allow the solvent to melt, followed by slow warming to ambient temperature. Initiation was generally observed at or near room temperature as evidenced by the formation of small white flakes that aggregated and precipitated as the polymerization proceeded. Adequate temperature control is necessary as the polymerizations are quite exothermic. After 20 minutes, the excess ethylene was vented in a fume hood, and the solid isolated and washed with acetone. Overall yield 1.08 g, 50% based on consumed monomer.

Polypropylene Method I. A thick walled reaction vessel was charged with **26** (18.3 mg, 27 μmol) and evacuated. A second thick walled reaction vessel was charged with titanocene and 9.3 mL of methylcyclohexane. Propylene (2.9 g, 68.9 mmol, 2600 equiv.) was condensed onto the titanocene at -196 °C. The resulting black solution of propylene/methylcyclohexane was allowed to warm to room temperature with stirring. The solution was cooled to -78 °C and trap-to-trap distilled into the cold (-196 °C) reaction vessel containing **26**.

An atmosphere of H_2 (≈ 73 equiv.) was admitted to the head space above the frozen solution. The reaction mixture was first allowed to thaw at -78 °C, then allowed to warm to room temperature with stirring. After 48 h, the reaction was halted by venting the remaining monomer and precipitating the polymer by addition of acidic methanol. Isolation of the polymer by filtration followed by drying in vacuo afforded 2.24 g of polypropylene, 77% based on consumed monomer.

Poly-1-pentene Method II. A thick walled reaction vessel was charged with **27** (16.0 mg, 29.7 μmol) and evacuated. 1-Pentene (9.6 g, 0.137 mol, 4600 equiv.) was added by vacuum transfer. The resulting pale yellow solution was stirred at ambient temperature for 7 days. The reaction became more viscous with time. The polymer was precipitated by addition of acidic methanol. The polymer was dissolved in diethyl ether and washed twice with small portions of water. Removal of the ether in vacuo yielded 4.7 g of a white waxy solid, 49% based on consumed monomer.

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